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Exotic superconductivity and magnetism in ruthenates

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Abstract. Basic experimental and theoretical results on ruthenates and rutheno-cuprates are reviewed. The electronic structure of various ruthenates and exotic superconductivity in Sr₂RuO₄ with spin-triplet pairing are described. The complex phase diagram of $Ca_{2-x}Sr_xRuO_4$, involving competing magnetic phases and metal-insulator transitions, is described, as are the exotic magnetic properties of Sr₃Ru₂O₇ and of the double perovskite Sr₂YRuO₆, and the coexistence of superconductivity and magnetism in the rutheno-cuprate RuSr₂GdCu₂O₈. Possible applications of Sr₂RuO₄ and SrRuO₃ are considered. The effect of strong electron correlations is discussed, and the properties of ruthenates and cuprates are compared.

1. Introduction

The term ruthenate denotes a large group of oxide materials based on ruthenium, and the best known of these is Sr₂RuO₄. The interest in ruthenates has seen an upsurge after the discovery of high-temperature superconductivity (HTSC) in the cuprates $La_{2-x}Sr_xCuO_4$ [1]. In addition to the fabrication of new Y-, Bi-, Tl-, and Hg-cuprates with a higher $T_{\rm c} \ge 100$ K, in 1987 a search for other superconducting

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materials not containing copper began worldwide. The earlier known oxide superconductor $Ba_{1-x}K_xBiO_3$ has a cubic structure, which differs from the layered structure of cuprates, and the similarities of, and differences between, this oxide and cuprates have been discussed by many researchers (e.g., see Ref. [2]). Among oxides isostructural with cuprates, Sr_2RuO_4 with $T_c \sim 1 \text{ K}$ proved to be the only known superconductor [3]. Being isostructural with the antiferromagnetic insulator La₂CuO₄, the ruthenate Sr₂RuO₄ exhibits no long-range magnetic order and does not require doping, i.e., possesses metallic and superconducting properties by itself, without any additives, in contrast to La₂CuO₄.

Initially it was assumed that the study of the ruthenate Sr₂RuO₄ would make it possible to clarify the HTSC mechanisms in cuprates. It was soon found, however, that the ruthenates form an extremely interesting class of materials by themselves. First, the superconductivity in Sr₂RuO₄ was found to be exotic, with triplet Cooper pairs with spin S = 1 and a finite orbital angular momentum, and exhibited a direct analogy with the superfluid phases of He-3. Second, it was found that there is strong competition of ferromagnetic, antiferromagnetic, orbital, and superconducting ordering, as well as metal-insulator transitions, which manifest themselves most vividly in the complex phase diagram of $Ca_{2-x}Sr_{x}RuO_{4}$. Third, the double-layered Sr₃Ru₂O₇ ruthenates constitute an example of a new class of quantum critical points where even at low temperatures the long-range magnetic order is suppressed by strong quantum fluctuations. Furthermore, the dielectric ruthenates with a double perovskite structure, Sr₂YRuO₆ [4], have long been known to have unusual magnetic properties. The ruthenium ions in them form an fcc lattice with an antiferromagnetic interaction between the nearest neighbors. In the Heisenberg model, such a system of spins is frustrated and its ground state is a spin liquid. Electron transport in systems with

frustrated spins could be a very interesting area of research. There are reports (so far not corroborated by other researchers) that signs of superconductivity below 60 K have been found in Cu-doped double perovskites Sr₂YRuO₆ [5]. Stabilization of the long-range antiferromagnetic order observed in double perovskites is possible only if there are additional weak perturbations, e.g., anisotropy. Fourth, not so long ago rutheno-cuprates RuSr₂GdCu₂O₈ (hybrid compounds that can be considered natural superlattices with alternating RuO₂ and CuO₂ layers separated by insulator buffer layers) were discovered. It was found that rutheno-cuprates exhibit coexistence of magnetism and superconductivity [5]. Fifth, ruthenates proved to be very interesting materials for applications: thanks to the high thermodynamic stability and the high metallic thermal conductivity, Sr₂RuO₄ can serve as a good substrate for HTSC films, while SrRuO₃ films could be used in the fabrication of ferroelectric devices. The main properties of ruthenates are listed in Table 1. In addition to stoichiometric compounds, solid solutions in which Ca substitutes for Sr are also intensively studied.

This zoo of ruthenates requires guidance, so to say. In October 2001, the first international conference on ruthenates and rutheno-cuprates was held in Salerno (Italy), with the present author being the only scientist from Russia. The aim of the present review is to introduce the readers of *Physics*-Uspekhi to a rapidly developing area of research in the physics of the condensed matter, and to its achievements and unsolved problems. In addition to cuprates and manganites, the system of ruthenates presents an example of competition of different magnetic, charge, orbital, and superconducting ordering, as well as various metal-insulator transitions. Undoubtedly, strong electron correlations, inherent in oxides of transition metals, are present in ruthenates, which constitutes an additional complication for the theory but also enriches the physics of the phenomena observed in such materials.

2. Exotic superconductivity in Sr₂RuO₄

Ruthenates form the Ruddlesden-Popper series $(Ca,Sr)_{n+1}Ru_nO_{3n+1}$ [7,8] (Fig. 1). At n = 1 we have a layered ruthenate Sr_2RuO_4 isostructural with the compound La_2CuO_4 (Fig. 1a), with the lattice parameters a = b = 3.8694 Å and c = 12.764 Å at room temperature [9]. At n = 2 a double-layered metallic metamagnet $Sr_3Ru_2O_7$ (Fig. 1b) forms. At n = 3 we have the compound $Sr_4Ru_3O_{10}$ (Fig. 1c). Finally, at $n = \infty$ SrRuO₃ has a distorted cubic perovskite structure. Actually, the double perovskite Ca_2YRuO_6 has the same structure as $SrRuO_3$, with a Y atom substituting for each second Ru atom. Let us begin our examination of the electronic structure of ruthenates with the best studied and most simple case of Sr_2RuO_4 .

2.1 Electronic structure

and the Fermi surface in $\mathrm{Sr}_2\mathrm{RuO}_4$

In contrast to the undoped antiferromagnetic insulator La₂CuO₄ with one hole localized on the copper atom in the $d_{x^2-y^2}$ orbital, the ruthenate Sr₂RuO₄ has four valence electrons of the Ru⁴⁺ ion that fill the t_{2g} states. As a result, the three t_{2g} bands formed with the participation of $(p-d)-\pi$ hybridized orbitals are filled to 4/3. Thus, the fact that this ruthenate has more than one band ensures that it is in a metallic state with a three-sheeted Fermi surface. In this sense Sr₂RuO₄ can be called a self-doped system, in contrast to La₂CuO₄.

Since the $(p-d)-\pi$ bond is weaker than the $(p-d)-\sigma$, the admixture of the oxygen p-states in ruthenates is smaller than in cuprates. For instance, the fraction of p-states near the Fermi level in Sr₂RuO₄ is 16%, while the fraction of Ru 4d-states amounts to 84% [10]. The band structure calculations of Sr₂RuO₄ by the LDA method [11, 12] have revealed the presence of three bands (α , β , and γ) that cross the Fermi level. Analytical expressions for the dispersion law of each band, $E_{\lambda}(k)$ ($\lambda = \alpha$, β , γ), were derived by the tight-

 Table 1. The most studied ruthenates and their electrical and magnetic properties.

Compound	Metal/insulator	Magnetism	Superconductivity
Sr ₂ RuO ₄	Metal, Fermi liquid	Exchange enhanced paramagnet	Triplet superconductor, $T_{\rm c} = 1.5 \ {\rm K}$
Ca ₂ RuO ₄	Mott – Hubbard insulator	Antiferromagnet $T_{\rm N} = 113 \ {\rm K}$	
Sr ₃ Ru ₂ O ₇	Metal, non-Fermi liquid	Metamagnet near a quantum critical point	? So far not discovered, is possible when sample quality is increased
Ca ₃ Ru ₂ O ₇	'Poor' metal	Antiferromagnet $T_{\rm N} = 56 \ {\rm K}$	Nonsuperconductor
SrRuO ₃	Metal, non-Fermi liquid	Ferromagnet $T_{\rm M} = 165 \ { m K}$	Nonsuperconductor
CaRuO ₃	'Poor' metal	Paramagnet near ferromagnetic instability	Nonsuperconductor
Sr ₂ YRuO ₆	Insulator	Antiferromagnet $T_{\rm N} = 26 \ {\rm K}$	_
RuSr ₂ GdCu ₂ O ₈	Metal	Magnetic material, $T_{\rm M} = 133$ K Ferromagnet? antiferromagnet? Possibly, a weak ferromagnet	Superconductor $T_{\rm c}^{\rm on} \sim 40 \ {\rm K}^*$
* T_c^{on} is the temperature of	the onset of the transition		



Figure 1. Unit cells of the first three terms of the Ruddlesden-Popper series.

binding method [10]. Here the index γ corresponds to the d_{xy} orbital, and α and β , respectively, to the bands formed by the d_{yz} and d_{zx} orbitals. The band structure of Sr₂RuO₄ is highly anisotropic, and dispersion along the *c* axis is small. For instance, the velocities on the Fermi surface are [12]

$$v_z = 1.4 \times 10^6 \text{ cm s}^{-1}, \quad v_x = 2.4 \times 10^7 \text{ cm s}^{-1}.$$

As a result, the Fermi surface has the shape of slightly corrugated cylinders, whose section by the basal plane is shown in Fig. 2. Here the hole α band forms an oblate cylinder centered at point $\mathbf{X} = (\pi/a, \pi/a)$, while the β and γ bands form electron cylinders centered at point Γ . The α and β bands are close to quasi-one-dimensional d_{yz} and d_{zx} , and their degeneracy is lifted due to the small value of the interband hopping integral, $t_{\perp} \approx 0.025$ eV [13]. Experimental studies of the Fermi surface in Sr₂RuO₄ by measuring the quantum oscillations of electrical resistivity (the Shubnikov–de Haas effect) and magnetic susceptibility (the de Haas–Van Alphen effect) fully corroborated the shape of the Fermi surface obtained in the band-structure calculations of [14, 15].

Despite the large difference in the resistivities along and across the RuO₂ planes, $\rho_c/\rho_{ab} \ge 500$, the temperature curves for both ρ_{ab} and ρ_c at T < 25 K are described by the Fermiliquid T^2 -law [3]. Deviations from the T^2 -law appear when T > 25 K. At high temperatures (T > 100 K), ρ_{ab} is approximately a linear function of T, while ρ_c decreases as T grows; such temperature behavior is a characteristic feature of cuprates, too.

Sr₂RuO₄ exhibits no long-range magnetic order, but its magnetic susceptibility is much higher than the Pauli susceptibility of free electrons, χ_0 . According to magnetic measurements [3], $\chi/\chi_0 = 7.3$, which suggests the presence of strong spin fluctuations. Indeed, calculation of the Stoner factor IN(0), where I is the exchange parameter at q = 0 and N(0) is the density of states at the Fermi level, produced the



Figure 2. Three cross sections of the Fermi surface of Sr₂RuO₄ in the basal plane of the body-centered tetragonal Brillouin zone [13].

following values:

IN(0) = 0.82 [11], IN(0) = 0.89 [13].

These values are close to the critical value IN(0) = 1, which determines the instability of a paramagnetic state under a transition to a ferromagnetic state in the band theory of magnetism (Stoner's criterion).

In SrRuO₃, the Stoner parameter IN(0) = 1.23 [16], so that Stoner's criterion is met and this ruthenate is a metallic ferromagnet with a magnetic moment $\mu = 1.6\mu_{\rm B}$ per formula unit and $T_{\rm c} = 150$ K [17–21]. The reason the Stoner parameter in the cubic crystal SrRuO₃ is larger compared to that in layered Sr₂RuO₄ lies in the stronger p-d hybridization and the greater contribution of the oxygen p-states into the density of states at the Fermi level, N(0).

More recent results of Mazin and Singh [22] show that in Sr₂RuO₄ not only are the ferromagnetic (FM) fluctuations strong, but so are the antiferromagnetic (AFM) fluctuations. Indeed, because of the quasi-two-dimensional nature of the α -and β -sections, the sheets of the Fermi surface are (if one ignores interband hybridization, i.e., $t_{\perp} = 0$) the parallel planes separated by the vector $2\pi/3a$ along the directions *x* and *y* (see Fig. 2). Such Fermi surfaces exhibit the property of nesting, leading to peaks in static magnetic susceptibility, which is at is maximum at the point $\mathbf{q} = \mathbf{Q} = (2\pi/3a, 2\pi/3a)$. The susceptibility of the itinerant electrons

$$\chi_0(q) = \sum_{kij} M_{ki,k+q,j} \frac{f_{\mathbf{F}}(\varepsilon_{k,i}) - f_{\mathbf{F}}(\varepsilon_{k+q,j})}{\varepsilon_{k+q,j} - \varepsilon_{k,i}}, \qquad (1)$$

where $f_F(\varepsilon_{ki})$ is the Fermi–Dirac distribution function for electrons of band *i*, and the matrix element $M_{ki,k+q,j}$ in the simplest approximation is assumed to be equal to 1 for the same bands (*i*, *j*) and to 0 for different bands, was written by Mazin and Singh [22] as

$$\chi_0(q) = N(0) + \chi_n(q) \,. \tag{2}$$

Here $\chi_n(q)$ denotes the contribution to susceptibility determined by nesting. It is common knowledge that these contributions are logarithmically large [23–25]. The total susceptibility in the random phase approximation is given by the formula

$$\chi(q) = \frac{\chi_0(q)}{1 - I(q)\,\chi_0(q)} = \frac{\chi_0(q)}{1 - I(q)\,N(0) - I(q)\,\chi_n(q)} \,. \tag{3}$$

If $I(Q)N(0) + I(Q)\chi_n(Q) > I(0)N(0)$, the AFM fluctuations are stronger than the FM fluctuations. The calculations of Mazin and Singh [22] show that I(0) N(0) = 0.82 and $I(Q) N(0) + I(Q) \chi_n(Q) = 1.02$, i.e., AFM fluctuations are stronger than FM fluctuations. In addition, these calculations suggest that a uniform paramagnetic state is unstable with respect to formation of a static spin density wave (SDW), with a tripling of the unit cell along the directions x and y, a feature not observed in experiments. Apparently, the rough approximation used for matrix elements leads to an overvaluation of $\chi_n(Q)$, but the conclusion that the Stoner parameter is close to 1 at q = 0 and $\mathbf{q} = \mathbf{Q}$ remains valid. The competition of FM and AFM fluctuations is such that not one type of long-range order has a chance of setting in. The fragility of the balance between these two types of fluctuations follows immediately from the fact that the substitution of an admixture of Ti (a nonmagnetic element) for ruthenium, i.e., $Sr_2Ru_{1-x}Ti_xO_4$, leads to the emergence of an FM state already at x > 2.5% [26].

Strong FM fluctuations were detected in observations of the Knight shift in the ¹⁷O NMR experiments [27]. A striking confirmation of Mazin and Singh's predictions [22] concerning strong AFM fluctuations with a vector $\mathbf{q} = \mathbf{Q} = (2\pi/3a, 2\pi/3a)$ was the discovery of an incommensurate peak with $\mathbf{q} = (0.6\pi/a, 0.6\pi/a, 0)$ in inelastic neutron scattering [28]. Thus, both theory and experiment suggest that there are strong, competing FM and AFM spin fluctuations in Sr₂RuO₄. The importance of these fluctuations for superconductivity will be discussed in Section 2.6.

2.2 Effects of strong electron correlations in Sr₂RuO₄

The success of band theory in predicting the shape of the Fermi surface and the peak with $\mathbf{q} = \mathbf{Q}$ in inelastic neutron scattering has led to the belief that Sr₂RuO₄ is a free-electron metal in which strong electron correlation (SEC) effects play no important role. However, it is very difficult to justify such a conclusion from the general viewpoint. Indeed, SEC effects are usually assumed to be insignificant if the kinetic energy of the electrons, whose measure is the band width W, is large compared to the Coulomb energy which can be characterized by the intratomic Hubbard matrix element U. For band widths $W_i \sim 1 \text{ eV}$, there is no reason for the inequality $W_i \ge U$ to be valid in Sr₂RuO₄. As for the value of the parameter U, at present there is no way it can be calculated directly from first principles. The one thing that is clear, however, is that for 4d-electrons the parameter U must be smaller than for the 3d-electrons. Since the mean radius of the 4d shell is twice as large as that of the 3d shell, a possible rough estimate is $U_{4d} = U_{3d}/2$. For the copper 3d-electrons in cuprates, the value of parameter U, according to estimates from different experiments, lies in the interval $U_{\rm Cu} \sim 4-8$ eV. Then for ruthenium one can expect that $U_{\rm Ru} \sim 2-4$ eV, which means that the electron system in Sr₂RuO₄ is in the intermediate correlation regime near the Mott-Hubbard transition point.

In addition to these general arguments, there are the following direct experimental indications of the presence of SEC effects in Sr_2RuO_4 :

(a) high values of the electron effective masses measured by the de Haas–Van Alphen method [14, 15], $m_{\alpha} = 3.4m_{e}$, $m_{\beta} = 6.6m_{e}$, and $m_{\gamma} = 12m_{e}$, where m_{e} is the free electron mass. Because of band structure effects, the mass of a band electron is greater than m_{e} , however, the experimental effective mass exceeds the calculated value by a factor of three to four. The same mass ratio follows from specific heat measurements [29]. A somewhat smaller value of the mass ratio, equal to 2.5, follows from the data on electron photoemission [30];

(b) suppression of the one-particle density of states in the low-energy region 0.5-2.5 eV below the Fermi level, which manifests itself in the valence-band photoemission spectra [31] (Fig. 3). This effect manifests itself most vividly in angleresolved photoemission spectra (ARPES), which make it possible to directly measure the band structure in quasi-twodimensional systems. Figure 4 shows the ARPES data for Sr₂RuO₄ [32] and the results of a band structure calculation [11]. Clearly, in the binding-energy interval from 0.5 to 3 eV there are several bands emerging from the calculation that do not appear in the experiments;

(c) the experimental value of the density of states at the Fermi level, N(0) [31], is three times smaller than the theoretical value obtained by the LDA method. Taking into



Figure 3. Spectra of UV (a) and X-ray (b) photoemission from the valence band of Sr_2RuO_4 for different incident-photon energies. The one-electron density of states [12] is shown for the sake of comparison. (After Ref. [31].)



Figure 4. Experimental band structure of Sr_2RuO_4 obtained in ARPES measurements. The large and small black dots indicate, respectively the strong and weak peaks in the ARPES data [32]. The dotted curves represent the theoretical band structure [11].

account self-energy corrections to the one-particle energies in the many-band Hubbard model [33] made it possible to lower N(0) to the experimental value. According to Pérez-Navarro et al. [33], Sr₂RuO₄ is a system with intermediate correlations, $U \sim W$;

(d) Inoue et al. [34] discovered in the photoemission spectra a low-energy satellite with a binding energy of 1.5 eV, which was interpreted by the researchers as a manifestation of the lower Hubbard band. Their data led to the estimate U = 2.4 eV, which together with the band width W = 1.4 eV yields U/W = 1.7. However, later this satellite was related to contamination of the sample's surface [31].

Thus, the gathered theoretical and experimental data suggest that SEC effects are undoubtedly present in ruthenates, but they manifest themselves not so strongly as they do in cuprates. For Sr₂RuO₄ one can expect the intermediate correlation regime, $U \sim W$, close to the Mott-Hubbard transition point. Below it is shown that the isoelectronic ruthenate Ca₂RuO₄ is already a Mott-Hubbard insulator. Another example of an isostructural and isoelectronic compound is Sr₂FeO₄, also an antiferromagnetic insulator. But how then is one to reconcile the conclusion that there are SECs with $U \sim W$ with the results of band theory discussed above in Section 2.1?

The point is that the achievements of band theory, such as the regular shape of the Fermi surface and the arrangement of susceptibility peaks in k-space, follow from the very fact that there is a Fermi surface, i.e., the Fermi-liquid properties of Sr_2RuO_4 . The LDA method accounts to a certain degree for the electron–electron Coulomb interaction, but becomes invalid for $U \gtrsim W$. The studies of the electronic structure of cuprates have shown that in the metallic optimally doped region, the Fermi surface obtained from first-principles LDA calculations coincides with the Fermi surface established through experiments [35]. However, the band widths and the dispersion far from the Fermi level do not coincide. Figure 4 also presents an example of how for Sr_2RuO_4 the experimental Fermi surface (to which SEC effects contribute) coincides with the result of an LDA calculation, but the band width in the experiment is much smaller than it is in band theory.

As for first-principles band-structure calculations that allow explicitly for SEC effects, several approaches to this problem have been developed, e.g., LDA + U [36], LDA-SIC [37], and LDA++ (LDA+ $U + \Sigma$) [38]. I believe that for $U \ge W$ the most suitable method is LDA++. Recently this method was used to obtain very convincing results in calculations of the electronic structure and magnetic properties of metallic iron: magnon dispersion [39] and the magnetization and susceptibility as functions of temperature above and below the Curie point [40] agree quantitatively with the results of experiments. The LDA++ method is based on a combination of first-principles LDA band-structure calculations and allowance for SECs in the dynamical meanfield theory (DMFT), specifically developed to describe SEC effects in the Hubbard model (see the reviews in Refs [41, 42]). The band structure calculation of Sr₂RuO₄ by the LDA++ method was done by Liebsch and Lichtenstein [43]. Their results for the dispersion law and the Fermi surface are represented in Fig. 5 which shows that the Fermi surface with allowance for correlations coincides with the Fermi



Figure 5. Quasiparticle band structure (a) and the Fermi surface (b) in Sr_2RuO_4 calculated by the LDA++ method [43]. The dots indicate the one-electron band structure calculated by the tight-binding method.

surface in the LDA calculation, but the band width with allowance for SEC effects is much smaller than in LDA. Note that in all these calculations the Coulomb matrix elements are adjustable parameters, and Liebsch and Lichtenstein [43] did their calculations with U = 1.2 eV and J = 0.2 eV, where J is the intratomic Hund exchange parameter.

2.3 Comparison of the structural properties of Sr₂RuO₄ and La₂CuO₄

Sr₂RuO₄ crystallizes in the K₂NiF₄-type structure, just as La₂CuO₄ does. For cuprates the structural phase transitions are known, hence, it is interesting to consider possible structural transitions in Sr₂RuO₄. For cuprates of the La_2CuO_4 family with the T-phase symmetry there is a number of low-temperature phases related to rotations of the CuO_6 octahedrons about axes that lie in the *ab* plane (the soft Σ_4 mode) [44]. Such rotations are characterized by octahedron tilting. At the same time, the rotations of octahedrons about the c axis (the rotational Σ_3 mode) do not lead to a structural transition in La₂CuO₄. However, the related family $R_2 CuO_4$ (R stands for a rare-earth element) with the T'-phase symmetry displays structural distortions caused by the rotations of the CuO_4 squares about the *c* axis [45]. Moreover, a similar type of structural distortion has been observed in Sr₂RhO₄ [46] and Sr₂IrO₄ [47], which are isostructural with La2CuO4 and Sr2RuO4.

Braden et al. [48] used the inelastic neutron scattering method to study the lattice dynamics of the Sr_2RuO_4 single crystals. The phonon dispersion laws for the three different types of vibrations along the [110] axis are shown in Fig. 6. Here the dots represent the experimental data and the solid curves the results of shell-model calculations. Clearly, there is no evidence of the Σ_4 mode instability, characteristic of La₂CuO₄. At the same time, there is a noticeable softening of the Σ_3 mode (rotations about the *c* axis) at the Brillouin



Figure 6. Low-frequency part of the phonon dispersion laws of different symmetry along the [110] direction of the Brillouin zone measured by inelastic neutron scattering on a Sr_2RuO_4 single crystal. There is clearly a softening of the rotational Σ_3 mode at the zone boundary [48].

zone boundary. Although the frequency of the respective vibrations decreases, it always remains finite, so that the Sr_2RuO_4 lattice is stable to vibrations of Σ_3 symmetry. Nevertheless, the temperature curves of the frequency and width of Σ_3 line are anomalous, in contrast to those of Σ_4 mode [48]. The frequency of Σ_3 mode only slightly depends on the q_z component, i.e., the rotational fluctuations about the *c* axis are clearly of a quasi-two-dimensional nature. Braden et al. [48] draw no definite conclusions concerning the reasons for the softening of Σ_3 mode. I believe that this may be another manifestation of Fermi-surface nesting, which contributes substantially not only to the magnetic susceptibility but also to the dielectric polarizability [49].

2.4 Basic properties of the superconducting state

In their report on superconductivity in Sr₂RuO₄, Maeno et al. [3] put the value of T_c at 0.93 K; the presence of superconductivity was established by the Meissner effect and by resistivity measurements for ρ_{ab} and ρ_c . The critical current density j_c measured at T = 0.32 K amounted to 2.0 A cm⁻² for the *ab* plane and 0.018 A cm⁻² along the *c* axis, and the anisotropy factor of j_c was 110. Measurements involved $2 \times 2 \times 0.1$ mm³ single crystals grown by the floating-zone method [50].

Later it was found (see Ref. [51]) that T_c strongly depends on the concentration of nonmagnetic impurities and crystal lattice defects. The best single crystals, grown at Kyoto University [52], are 4-cm large. In these crystals, the mean free path of the electrons $l \sim 2000$ nm and $l/\xi = 30$, so that the 'clean' limit is attained. The maximum value of T_c that has been obtained so far is 1.489 K. Figure 7 shows the behavior of T_c as a function of the residual resistivity ρ_0 found from the temperature dependence of the resistivity $\rho = \rho_0 + AT^2$ in the 4.2-25-K interval. The magnitude of ρ_0 is determined by the lattice defect concentration (open circles with numbers from 1 to 10) and the Al impurity (black circles, the data of Mackenzie et al. [53]). The solid curve in Fig. 7 represents the fit of Mackenzie et al. [53] to the Abrikosov–Gor'kov theory for pair destruction by magnetic impurities [54].



Figure 7. T_c plotted as a function of the residual resistivity ρ_0 in Sr₂RuO₄; the numbers correspond to the different samples from Ref. [51], and the solid curve corresponds to the results that follow from the modified Abrikosov–Gor'kov theory.

A study of the temperature dependence of the critical field H_{c2} for Sr₂RuO₄ samples done by Mao et al. [51] led to the following relationship:

$$H_{c2,||c}(0) = aT_c^2, (4)$$

where a = 0.029 T K⁻². Using the Ginzburg–Landau formula for three-dimensional anisotropic superconductors,

$$H_{c2,||c}(0) = \frac{\phi_0}{2\pi\xi_{ab}(0)^2},$$
(5)

where ϕ_0 is the magnetic flux quantum, and $\xi_{ab}(0)$ is the coherence length in the *ab* plane, we can establish the relationship between the experimental values of $\xi_{ab}(0)$ and T_c :

$$\xi_{ab}(0) = \left(\frac{\phi_0}{2\pi a}\right)^{1/2} \frac{1}{T_c} \,. \tag{6}$$

Both the data of Mao et al. [51] and the data of earlier research [55, 56] satisfy this relationship. To find the mean free path *l* from measurements of the residual resistivity ρ_0 , the researchers used the formula

$$l = \frac{2\pi\hbar d}{e^2 \rho_0 \sum_i k_{\rm F}^i} \,,\tag{7}$$

where d = 6.4 Å is the layer separation, and the sum of $k_{\rm F}$ over the three sections α , β , and γ of the Fermi surface is known from measurements of de Haas–Van Alphen quantum oscillations. Thus, *l* can be related to ρ_0 and, through Fig. 7, to $T_{\rm c}$. On the other hand, Eqn (6) relates ξ_{ab} and $T_{\rm c}$. As a result, Mao et al. [51] obtained the relationship between $\xi_{ab}(0)$ and the mean free path (Fig. 8). The curve representing this relation differs markedly from the curve for conventional BCS superconductors,

$$\frac{1}{\xi_{\rm P}} = \frac{1}{\xi_0} + \frac{1}{\beta l} \,, \tag{8}$$

where ξ_0 is the inherent coherence length; from Fig. 8 it follows that $\xi_0 \approx 720$ Å. In equation (8), the constant β is of



Figure 8. Correlation length $\xi_{ab}(0)$ plotted as a function of the mean free path *l*. The lower (dashed) curve represents the dependence of $\xi_{ab}(0)$ on *l* for an ordinary superconductor of the BCS type [51].

order unity, and the Pippard coherence length $\xi_{\rm P}$ is comparable to $\xi_{\rm GL}(0)$. According to equation (8), $\xi_{ab}(0)$ decreases with *l*, which contradicts the experimental data on Sr₂RuO₄.

The temperature dependence of $H_{c2,||c}$ for Sr₂RuO₄ also differs from the BCS type. For conventional superconductors of the s type, $H_{c2}(T)$ only slightly (by several percentage points) differs from the T^2 -law. For Sr₂RuO₄ the difference exceeds 10% [51].

Thus, a thorough analysis of the dependence of T_c and the electrical and magnetic properties of Sr_2RuO_4 on the concentration of nonmagnetic defects and temperature points to the difference between the superconducting state of Sr_2RuO_4 and that of a typical BCS superconductor. There are also direct experimental indications of the exotic nature of the superconducting state in Sr_2RuO_4 , which will be discussed in the next section.

2.5 Symmetry of the order parameter in Sr₂RuO₄

Even before the necessary direct experiments were conducted, the possibility of a spin-triplet superconducting state in Sr₂RuO₄ was predicted theoretically by Rice and Sigrist [57]. The researchers based their reasoning on the experimental data of Maeno et al. [3] on the large enhancement of the paramagnetic susceptibility in comparison to the Pauli susceptibility, on the presence of a ferromagnetic state in SrRuO₃, and on the assumption concerning the role of Hund exchange in the formation of S = 1 triplet states of two holes on the (d_{yz} , d_{zx}) orbitals. They examined the triplet superconductivity of a square lattice that was considered to be an electron analog of the superfluid A-phase in ³He.

As is known (e.g., see Ref. [58]), in the case of spin-triplet pairing, the wave function of the pair can be written as a matrix in the spin space:

$$\Psi' = g_1(k)|\uparrow\uparrow\rangle + g_2(k)(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) + g_3(k)|\downarrow\downarrow\rangle = \begin{pmatrix} g_1(k), g_2(k) \\ g_2(k), g_3(k) \end{pmatrix},$$
(9)

where the eigenstates of the operator S^z with projections +1, 0, and -1 have the form

$$|\uparrow\uparrow\rangle = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \quad |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad |\downarrow\downarrow\rangle = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}.$$

The other way to express the wave function of the spin-triplet pair is to use the base system of spin matrices:

$$\mathbf{i}\boldsymbol{\sigma}\sigma_y = (\mathbf{i}\sigma_x\sigma_y,\,\mathbf{i}\sigma_y\sigma_y,\,\mathbf{i}\sigma_z\sigma_y)$$

i.e.,

$$\Psi^{I} = \mathbf{i} \left(\mathbf{d}(k) \cdot \mathbf{\sigma} \right) \sigma_{y} = \begin{pmatrix} -d_{x}(k) + \mathbf{i}d_{y}(k), & d_{z}(k) \\ d_{z}(k), & d_{x}(k) + \mathbf{i}d_{y}(k) \end{pmatrix}.$$
(10)

The components of vector **d** can be linearly expressed in terms of the amplitudes $g_{\alpha}(\mathbf{k})$:

$$g_1 = -d_x + id_y, \quad g_2 = d_z, \quad g_3 = d_x + id_y.$$

Pauli's exclusion principle forces the orbital part of the wave function with S = 1 to be spatially odd, so that the orbital quantum number *l* in Eqn (9) takes on only odd values: l = 1, 3, Accordingly, only p, f, ... pairing is possible. In the case of p pairing, both the amplitudes $g_{\alpha}(k)$ and the vector $\mathbf{d}(\mathbf{k})$ are odd functions of \mathbf{k} : $g_{\alpha}(-k) = -g_{\alpha}(k)$, $\mathbf{d}(-\mathbf{k}) = -\mathbf{d}(\mathbf{k})$. In a tetragonal crystal, the parameter $\mathbf{d}(\mathbf{k})$ must transform by one of the odd irreducible representations, among which are four one-dimensional representations and one twodimensional representation [57, 58]. To clarify the gap symmetry still further, we turn to experimental data. Information about the spin state of the order parameter is usually extracted from measurements of the Knight shift in NMR experiments and data on the scattering of polarized neutrons, while information about the orbital state is extracted from measurements of the muon spin resonance (μ SR) and the symmetry of the vortex lattice.

Measurements of the Knight shift on ruthenium nuclei below $T_{\rm c}$ are extremely complicated in view of the small value of the gyromagnetic ratio for $^{101}\mathrm{Ru},~^{101}\gamma =$ 0.2993 MHz kOe⁻¹, which requires the use of strong external fields exceeding the critical fields $H_{c2,||c}(0) = 0.75$ kOe and $H_{c2,||ab}(0) = 15$ kOe. Hence the NMR experiments were conducted on the nuclei of the oxygen isotope ¹⁷O (nuclear spin I = 5/2) substituting for the isotope ¹⁶O (I = 0). Figure 9 shows the temperature dependence of the Knight shift for NMR on ¹⁷O in a magnetic field H = 6.5 kOe parallel to the RuO₂ plane [59]. Within experimental errors, no changes in $T_{\rm c}$ were found, which proves that spin-triplet pairing is present in Sr₂RuO₄. Unfortunately, because of the small value of $H_{c2,||c}$ it proved impossible to measure the NMR signal in a field normal to the RuO₂ plane. Measurements of the scattering of polarized neutrons [60] also provide the definitive identification of Sr₂RuO₄ as a spin-triplet superconductor.

Time-reversal symmetry breaking in the superconducting state was detected by the increase in the rate of muon spin relaxation below T_c [61]. This experiment isolates the order



Figure 9. Temperature dependence of the Knight shift in ¹⁷O NMR measurements in Sr_2RuO4 , which proves the spin-triplet pairing of the Cooper pairs. The dashed curve represents the results of the BCS theory for singlet pairing [59].

parameter E_u with $S_z = 0$ and $l_z = \pm 1$ (the chiral p-wave):

$$\mathbf{d}(\mathbf{k}) = \hat{z} \Delta_0(k_x \pm \mathrm{i}k_y), \quad \hat{z} \equiv |S_z = 0\rangle.$$
(11)

The amplitude of such a gap is isotropic, $\Delta(k) = \Delta_0(k_x^2 + k_y^2)^{1/2}$, and the gap never vanishes in the cylindrical Fermi surface in Sr₂RuO₄. Such behavior, however, contradicts the results of a number of experiments, which point to the presence of a line of zeros in the superconducting state. Among these results are the power-law, as $T \rightarrow 0$, temperature dependence of (a) the specific heat, $C(T) \sim T^2$ [62, 63], (b) the relaxation rate in nuclear quadrupole resonance, $T_1^{-1} \sim T^3$ [64], (c) thermal conductivity, $\varkappa(T) \sim T^2$ [65, 66], (d) the penetration depth [67], and (e) electronic ultrasound attenuation [68].

Several modifications of the symmetry of the order parameter have been proposed in order to resolve these contradictions: an anisotropic p-gap [69] or f-gap of the type

$$\mathbf{d}(\mathbf{k}) = \hat{z} \varDelta_0(k_x \pm \mathrm{i}k_y) g(\mathbf{k}) \,, \tag{12}$$

where $g(\mathbf{k})$ is an even function of k, that vanishes at certain values of k, e.g., $g(k) = k_x k_y$ or $g(k) = k_x^2 - k_y^2$ [70–72]. Both variants of the f-gap have a vertical zero line along the k_z axis, which should lead to a strong fourfold anisotropy of thermal conductivity $\varkappa(\theta, H)$ in a magnetic field, where θ is the polar angle in the *ab* plane measured from the direction of field H. However, measurements of $\varkappa(\theta, H)$ for a field H parallel to the *ab* plane revealed a fairly weak anisotropy [65, 66], which suggests that the zero line in the superconducting gap of Sr₂RuO₄ is horizontal.

Recently Zhitomirsky and Rice [73] proposed a mechanism for the formation of a horizontal zero line allowing for the orbital structure of the superconducting state emerging because of the existence of many bands in Sr₂RuO₄. The point is that, due to the many-band nature of the Fermi surface, the magnetic fluctuations which lead to spin-triplet pairing [16, 22] exhibit strong orbital dependence, which manifests itself, say, in NMR measurements [27]. As noted by Agterberg et al. [74], the different symmetries $\{xy\}$ and $\{yz, zx\}$ of the Fermi surface sheets with respect to $z \rightarrow -z$ reflections lead to suppression of the interband scattering of the Cooper pairs within one RuO₂ plane. This means that only one band plays an active role in the formation of superconductivity, while in the second band superconductivity is induced by weak higher-order perturbations, such as interplanar interband transitions. Then in the second band the gap Δ_2 and the intrinsic critical temperature $T_{c2}^{(0)}$ are small, which for finite temperatures will lead to the observed nonzero density of states at the Fermi level followed by a crossover, as $T \rightarrow 0$, to the state with a nonzero gap. Of course, because of interband transitions there emerges a peculiar proximity effect in k-space, and $T_{\rm c}$ has one value for the entire crystal; nevertheless, the idea that there are active and passive bands with respect to pairing can be verified through experiments.

The point is that for the γ -band of $\{xy\}$ symmetry, the density of states at the Fermi level is enhanced due to a Van Hove singularity in the [100] direction, while for the α - and β -bands of $\{yz, zx\}$ symmetry the effective (angle-dependent) density of states is greater in the [110] direction [22, 75]. According to Agterberg's calculations [75], for p pairing to occur, the Abrikosov vortex lattice in the mixed state with H||z must be a square lattice with the axes oriented along [100] or [110], depending on the anisotropy of the in-plane

component of the field H_{c2} . The neutron diffraction measurements conducted by Riseman et al. [76] corroborated the assumption that the vortex lattice in Sr₂RuO₄ is square (Fig. 10). Furthermore the symmetry of the diffraction pattern enabled the researchers to conclude that the γ -band contributes the most to the formation of superconductivity. Interestingly, the measurement described in Ref. [76] revealed that even for the weakest external field H = 5 mT and a neutron wavelength of 30 Å the distance between the vortices is fairly large: 0.64 μ m. The fact that the γ -band proved to be the active band can easily be explained, since for this band the spin-fluctuation interaction can be expected to be the strongest. It is for the γ -band that the experiments [14] on the de Haas – Van Alphen effect yield the greatest value of the effective mass (see Section 2.2). The band structure calculations [72] of partial contributions to the spin susceptibility also show that the γ -band provides the greatest contribution. Despite the fact that nesting with $\mathbf{Q} = (2\pi/3a, 2\pi/3a, 0)$ is initially related to the quasi-one-dimensional α - and β -bands, the existing weak hybridization of the α -, β -, and γ -bands is sufficient for the contribution from nesting to enhance the partial susceptibility of the γ -band.

The two-band model of superconductivity with an active band 1 (γ -band) and a passive band 2 (α - and β -bands) was examined by Zhitomirsky and Rice [73]. For band 1 the gap has no zeros on the Fermi surface,

$$d_1(\mathbf{k}) \sim (\sin k_x a + \sin k_y a) \,. \tag{13}$$

Due to the interplanar interband scattering of Cooper pairs, the pairing in band 1 induces a gap in band 2:

$$d_2(\mathbf{k}) \sim \left(\sin\frac{k_x a}{2}\cos\frac{k_y a}{2} + \sin\frac{k_y a}{2}\cos\frac{k_x a}{2}\right)\cos\frac{k_z c}{2}.$$
(14)



Figure 10. The pattern of neutron diffraction on an Abrikosov vortex lattice in Sr_2RuO_4 [76]. The crystal axes *a* and *b* coincide with the horizontal and vertical axes in the figure.

The gap $d_2(\mathbf{k})$ has a horizontal zero line at $k_z = \pm \pi/c$. What is important is that the zero line is retained under a small admixture of gap (13) to the gap (14), with only the position of the zeros along the k_z axis being shifted slightly. The matrix elements of intraband and interband pairing were selected in the form

$$V_{11}(\mathbf{k}, \mathbf{k}') = -g_1 f(\mathbf{k}) f(\mathbf{k}'), \quad f(\mathbf{k}) = \frac{\mathbf{k}}{k_{\rm F}}, \quad (15)$$

$$V_{22}(\mathbf{k}, \mathbf{k}') = -g_2 \tilde{f}(\mathbf{k}) \tilde{f}(\mathbf{k}'), \quad \tilde{f}(\mathbf{k}) = \sqrt{2} \frac{\mathbf{k}}{k_{\rm F}} \cos \frac{k_z c}{2},$$

$$V_{12}(\mathbf{k}, \mathbf{k}') = -g_3 f(\mathbf{k}) \tilde{f}(\mathbf{k}').$$

The interaction in the active band is attractive $(g_1 > 0)$, with the parameters g_2 and g_3 assuming any sign. The densities of states at the Fermi level are distributed according to the results of measurements [14] of the de Haas–Van Alphen effect:

$$rac{N_1^{(0)}}{N_2^{(0)}} = rac{N_{\gamma}(0)}{N_{lpha}(0) + N_{eta}(0)} = rac{0.57}{0.43} \, .$$

Calculation of the specific heat in the two-band model [73] yielded

$$C(T) = 2\sum_{k,l} E_{k,l} \frac{df(E_{k,l})}{dT},$$
(16)

where $E_{k,l} = \sqrt{\epsilon_{kl}^2 + \Delta_l^2(k)}$ stands for the quasiparticle energy in the band l = 1, 2, and f(E) is the respective Fermi distribution. The results of the calculation are shown in Fig. 11. Note that at $g_2/g_1 = 0.85$ the ratio of the effective coupling constants is $\lambda_2/\lambda_1 = g_2N_2(0)/g_1N_1(0) = 0.64$, while the ratio of T_c in the passive and active bands is

$$\frac{T_{c,\alpha\beta}^{(0)}}{T_{c,\gamma}^{(0)}} = 0.086.$$
(17)

The field dependence of the residual density of states at low temperatures is also described by the two-band model. Even a weak magnetic field $H \ll H_{c2}$ rapidly restores up to 40% of the total density of states [63]. Such behavior can be explained by suppression of superconductivity in the passive α - and β -bands, with curve 4 in Fig. 11 corresponding to this case. Thus, the two-band model with the active γ -band and the passive α , β -band makes it possible, due to the proximity effect in k-space, to describe the triplet state with a horizontal zero line in the gap $\Delta_{\alpha,\beta}^{(k)}$ and with a gap $\Delta_{\gamma}(k) = \Delta_0(\sin k_x + \sin k_y)$ that does not vanish on the Fermi surface.

2.6 Comparison of superconductivity in the ruthenate Sr_2RuO_4 and in cuprates

Despite the close similarity of the crystal structures, the difference in the orbitals near the Fermi level leads to a large difference in the electronic structures and, as a result, in the nature of spin fluctuations. The spin fluctuations in both systems are large, but while in metallic cuprates in the region of light and optimal doping the antiferromagnetic fluctuations are very evident, in ruthenates there is significant competition between ferromagnetic and antiferromagnetic fluctuations. According to Mazin and Singh [22], AFM fluctuations dominate in Ca₂RuO₄; still, spin-triplet super-



Figure 11. Temperature dependence of the specific heat in the two-band model of Sr_2RuO_4 . The upper panel shows the theoretical results with the following parameters: $g_2/g_1 = 0.85$ and $g_3/g_1 = 0.01, 0.07, 0.20$ for curves I-3, respectively. Curve 4 corresponds to the case where $g_2/g_1 = 0.1$ and $g_3/g_1 = 0.07$. In the lower panel the circles represent the experimental data gathered by Nishizaki et al. [62], and the solid curve is curve 2 from the upper panel. Also shown are the results of calculation in the single-band model: an anisotropic gap with a line of zeros (dashed curve) and an isotropic gap (dot-dash curve) [73].

conductivity is induced by FM fluctuations. Electron correlations also exist in both systems, although in cuprates they are probably stronger than in ruthenates. To establish the reason for such a great difference in the values of T_c in cuprates and in the ruthenate Sr₂RuO₄, in Ref. [77] the magnetic mechanism of pairing was examined within the t-J-I-model.

For cuprates, the t-J model emerges as the effective lowenergy model describing the motion of a hole against the background of AFM fluctuations [78]. In the ruthenate Sr₂RuO₄, bearing in mind the activity of the γ -band, we can also consider the motion of a carrier against the background of FM fluctuations in the single-band model. Since local twoparticle states ('doublets') are disadvantageous (because of SEC effects), it has proved convenient to represent the Hamiltonian of the model in terms of the Hubbard X-operators:

$$H = \sum_{f\sigma} (\varepsilon - \mu) X_f^{\sigma\sigma} - t \sum_{f\delta\sigma} X_f^{\sigma 0} X_{f+\delta}^{0\sigma}$$
$$+ J \sum_{f\delta} K_{f,f+\delta}^{(-)} - I \sum_{f\delta} K_{f,f+\delta}^{(+)} , \qquad (18)$$
$$K_{fg}^{(\pm)} = \mathbf{S}_f \cdot \mathbf{S}_g \pm \frac{1}{4} n_f n_g .$$

Here the Hubbard operators $X_f^{pq} = |f, p\rangle \langle f, q|$ are defined on a reduced Hilbert space containing empty states $|0\rangle$ and oneelectron states $|\sigma\rangle$ ($\sigma = \uparrow$ and $\sigma = \downarrow$) at each site f. The constraint on two-particle states is given by the condition that

$$X_f^{\uparrow\uparrow} + X_f^{\downarrow\downarrow} + X_f^{00} = 1.$$
⁽¹⁹⁾

The operators S_f and n_f in Eqn (18) are the operator of spin and the operator of the number of particles at site f, and the vector δ connects the nearest neighbors.

The t-J-I model for Sr₂RuO₄ emerges from an examination of the many-band electronic structure in the strong correlation limit. This model will be discussed in Section 3. It is assumed that SECs split the γ -band into a filled lower Hubbard band (LHB) with $n_e = 1$ and a partially filled upper Hubbard band (UHB) with $n_e = n_0$. The passive α - and β -bands serve, within such an approach, as a reservoir that ensures the presence of two holes per formula unit in the sum over the three bands. To make the comparison with cuprates easier, the authors of Ref. [77] use a hole representation. Then the electrons at the bottom of the UHB transform into holes at the top of the hole LHB with a hole concentration $n_h = 1 - n_0$. For cuprates the carriers are the holes at the top of the electron LHB with an electron concentration $n_e = 1 - n_0$. In the case of La_{2-x}Sr_xCuO₄ $n_0 = x$.

In the mean-field approximation for systems with SECs [79], the authors of Refs [77, 80] studied the superconducting states with s, p, and d symmetries. An important feature of systems with SECs is that, in addition to satisfying ordinary self-consistency equations for the gap and the chemical potential, all solutions must satisfy the constraint (19) which in the superconducting phase leads to the following condition:

$$\frac{1}{N}\sum_{k}\left\langle X_{-k}^{0\downarrow}X_{k}^{0\uparrow}\right\rangle =0\,,\tag{20}$$

which means that the amplitude of the wave function of a pair at a single site is zero. An isotropic gap of the s type does not meet the condition (20), but states with p and d symmetries do. The gap is given by the following formula:

$$\Delta_{kl} = \alpha_l \psi_l(k) \frac{1}{N} \sum_p \psi_l(p) \frac{B_p}{c(n_0)} , \qquad (21)$$

where l = p or d, and the coupling constants and the angular parts are

$$\begin{aligned} \alpha_{\rm p} &= \lambda, \quad \psi_{\rm p}(k) = \frac{1}{2} \left(\sin k_x + \mathrm{i} \sin k_y \right), \\ \alpha_{\rm d} &= \left(2g - \lambda \right), \quad \psi_{\rm d}(k) = \frac{1}{2} \left(\cos k_x - \sin k_y \right). \end{aligned} \tag{22}$$

Here

$$\lambda = \frac{I}{t}, \ g = \frac{J}{t}, \ \omega_p = -\frac{1}{z} \sum_{\delta} \exp(ip\delta),$$

z is the number of nearest neighbors, $B_p = \langle X_{-p}^{0\downarrow} X_p^{0\uparrow} \rangle$, and $c(n_0) = (1 + n_0)/2$. The self-consistency equation for the gap is similar to the equation of BCS theory with angular anisotropy:

$$\frac{1}{\alpha_l} = \frac{1}{N} \sum_p \frac{\psi_l^2}{2E_{pl}} \tanh\left(\frac{E_{pl}}{2\tau}\right),\tag{23}$$

where $E_{pl} = [c^2(n_0)(\omega_p - m)^2 + \Delta_{pl}^2]^{1/2}$, and *m* is the dimensionless chemical potential, also determined in a self-consistent manner. The numerical solution of equation (23) at $T = T_c$ and $\Delta = 0$ is shown in Fig. 12, where the dimensionless coupling constants in the p and d coupling channels (i.e., in Sr₂RuO₄ and cuprates) were selected numerically equal. As a result, the difference in the values of T_c by a factor of 100 emerges only thanks to the different gap anisotropies which, in turn, emerge because of the opposite signs of the effective interaction. An analytical investigation of the equations for $T_{\rm c}$ done in Ref. [77] shows that in the case of p-type symmetry the Van Hove singularity contributes nothing to the increase in $T_{\rm c}$, since in the effective density of states, the corresponding small electron velocity on the Fermi surface and the angular part of $\psi_{n}(k)$ cancel out. On the other hand, for the d channel there is no such canceling out of the angular part of $\psi_{d}(k)$, with the result that the effective density of states has the Van Hove singularity which drives T_c up.

Thus, the results of a comparison of the superconductivity in the ruthenate Sr_2RuO_4 and cuprates within a single model suggest that two factors are responsible for the high values of T_c in cuprates: strong AFM fluctuations in the system of strongly correlated carriers, and the presence of the Van Hove singularity. Earlier Dagotto et al. [82] arrived at a similar conclusion for cuprates. Among the theoretical papers on spin-triplet superconductivity I would also like to mention Ref. [83], where a Fermi liquid that is almost perfectly localized due to SEC effects is examined in the two-band model with triplet pairing caused by local Hund exchange, which is very close in essence to the initial ideas of Rice and Sigrist [57] about the reasons for triplet pairing.



Figure 12. Concentration dependence of T_c for p pairing in ruthenates and d pairing in cuprates. Here the coupling constants are $\lambda_p = I/t$ and $\lambda_d = 2J/t$ [81].

3. Properties of the solid solutions $Ca_{2-x}Sr_{x}RuO_{4}$

Initially ruthenate studies focused on the nearly ferromagnetic metal Sr_2RuO_4 and the ferromagnetic metal $SrRuO_3$. It was assumed that in ruthenates, in contrast to cuprates (with strong antiferromagnetic correlations), one is dealing with ferromagnetic correlations. However, the discovery of antiferromagnetism in Ca₂RuO₄ and the subsequent discovery of a complicated set of structural, magnetic, and electronic transformations in $Ca_{2-x}Sr_xRuO_4$ showed that the situation with ruthenates is much more complex and interesting than was assumed initially.

3.1 Structural, magnetic,

and electronic transitions in Ca2RuO4

The first samples of Ca₂RuO₄ were synthesized by Nakatsuji et al. [84] and Cao et al. [85]. This substance differs from Sr₂RuO₄ by the way in which RuO₆ octahedrons are oriented [86], as is often the case with perovskite-like crystals [87]. The very first magnetic measurements involving polycrystals [84] excluded the possibility of ferromagnetic ordering: antiferromagnetism was discovered in Ca₂RuO₄, with a possible small ferromagnetic moment caused by sublattice canting. Neutron diffraction measurements [86] involving polycrystalline Ca₂RuO₄ samples also confirmed the presence of AFM order below $T_N = 110$ K.

Two research groups reported their results of studies involving Ca₂RuO₄ single crystals, with the magnetic properties differing very little but the electrical properties differing substantially. Cao et al. [85] grew the Ca₂RuO₄ single crystals by the self-flux technique [88], while Fukazawa et al. [89] grew the Ca₂RuO₄ crystals by the same technique used by Lichtenberg et al. [50] to grow Sr₂RuO₄ single crystals, the floating-zone method. According to Cao et al. [85], Ca₂RuO₄ has $T_{\rm N} = 110$ K and an easy axis of magnetization in the *ab* plane, with the saturation magnetic moment μ_{s} amounting to $0.4\mu_{\rm B}$ per ruthenium ion even in a strong magnetic field of 30 T, which is much smaller than the value of $2\mu_{\rm B}$ expected for S = 1. According to the neutron diffraction data for polycrystalline Ca2RuO4, the sublattice magnetic moment $m = 1.3 \mu_{\rm B}$ [86]. The measurements of the magnetic susceptibility of single crystals done by Fukazawa et al. [89] showed that $T_{\rm N} = 113$ K and that the easy axis of magnetization lies along the [010] direction. For both batches of single crystals, Cao et al. [85] and Fukazawa et al. [89] noted that the susceptibility is not described by the generalized Curie-Weiss law. Both teams corroborated the presence of sublattice canting and attributed it to the Dzyaloshinskii-Moriya interaction [90] induced by structural distortions in the RuO₂ layer.

The resistivity measurements done by Cao et al. [85] revealed the nonmetallic behavior of $\rho_{ab}(T)$ over the 70–300-K range with $d\rho/dT < 0$ and a decrease in ρ by eight orders of magnitude as the temperature increased from 70 K to 300 K. Here $\rho(T)$ is not described by an activation dependence in the entire temperature range, and only in the high-temperature range 220 K < T < 290 K can an activation gap $E_g = 0.2$ eV be introduced. A dependence that provides a better description of the behavior of $\rho(T)$ in the entire temperature range is

$$\rho(T) = A \exp\left(\frac{T_0}{T}\right)^{\beta},\tag{24}$$

characteristic of hopping conduction with variable-range hopping, while the exponent $\beta = 1/2$ is characteristic of three-dimensional hopping with allowance for electron correlations [91]. Hopping conduction without correlations with $\beta = 1/4$ [92] agrees poorly with the experimental temperature dependence of ρ . According to Cao et al. [85], there is neither jump nor kink in the $\rho(T)$ curve.

The temperature dependence of the resistivity ρ_{ab} in Ca₂RuO₄ single crystals was measured by Fukazawa et al.

[89] in the 150-300-K range and was found to agree well in the entire temperature range with an activation dependence with a gap $E_g = 0.2$ eV. Important differences in the samples used by Cao et al. [85] and Fukazawa et al. [89] also manifested themselves in the temperature dependence of the specific heat: in the 1-20-K range the specific heat [85] is described by the formula

$$\frac{C(T)}{T} = \gamma + bT^2, \qquad (25)$$

where from the point of intersection of the curve with the *y*-axis it was found that $\gamma = 4 \text{ mJ mol}^{-1} \text{ K}^{-2}$, which points to the nonzero density of states at the Fermi level. Similar measurements done for Sr₂RuO₄ yielded $\gamma =$ $= 45 \text{ mJ mol}^{-1} \text{ K}^{-2}$. On the other hand, similar measurements done by Fukazawa et al. [89] in the 1.8-15-K range yielded $\gamma = 0 \pm 1 \text{ mJ} \text{ mol}^{-1} \text{ K}^{-2}$ for $\text{Ca}_2 \text{RuO}_4$ and $\gamma = 39 \pm 1 \text{ mJ mol}^{-1} \text{ K}^{-2}$ for Sr₂RuO₄ [3]. Thus, different samples were found to exhibit marked differences in their electronic properties with respect to both resistivity and specific heat: a 'poor' disordered metal with SEC effects [85], and a Mott-Hubbard insulator [89]. The reasons for these differences probably stem from the technologies used in growing the single crystals. In the floating-zone method [50], the crystal in the process of growing is not in contact with the crucible, which guarantees high purity of the crystal (surely the mean free path l = 2000 nm in Sr₂RuO₄ is proof of that; see Section 2.4). Probably, the Ca₂RuO₄ samples used by Cao et al. [85] had defects in the stoichiometry or a small admixture of impurities, which results in a small number of carriers at the Fermi level.

While Sr_2RuO_4 and $SrRuO_3$ are structurally stable, due to the large difference in the ion radii in calcium ruthenates (1.04 Å for Ca^{2+} and 1.20 Å for Sr^{2+}) the probability of excess oxygen appearing in the interstitial sites may be substantial (just as it is in $La_2NiO_{4+\delta}$ [94]). Even small variations of the excess-oxygen concentration change the pattern of structural phase transitions in $Ca_2RuO_{4+\delta}$, which was thoroughly studied by Braden et al. [86], who used the neutron diffraction method. Two groups of Ca_2RuO_4 polycrystals were prepared for the neutron diffraction studies: stoichiometric samples, which Braden et al. [86] denoted S-Ca₂RuO₄ (the parameter c = 11.94 Å), and samples with excess oxygen, O-Ca₂RuO₄ (c = 12.35 Å). The stoichiometric samples were partially deoxidized from O-Ca₂RuO₄ through annealing at 900 °C in air and rapid cooling. Note that in the single crystals used by Cao et al. [85], c = 12.1250 Å, which confirms their nonstoichiometric nature.

At room temperature, the structure of S-Ca₂RuO₄ differs from the ideal K₂NiF₄-type structure in that it contains strong orthorhombic distortions which get stronger as the temperature drops. The group-theoretical diagram of possible distortions in the initial K₂NiF₄-type structure and the respective rotations of the RuO₆ octahedrons are shown in Fig. 13. The phase with the Acam structure (Cmca in standard notation) is obtained through freezing rotations about the c axis by an angle φ . As noted earlier in Section 2.3, Sr_2RuO_4 shows a tendency toward such instability. The phases Abma (Cmca) and P42/ncm are known as the LTO and LTT phases in cuprates [95, 96] and are obtained through rotations of the octahedron by an angle θ about the axes that are in the ab plane. The structure of S-Ca₂RuO₄ is *Pbca*-symmetric with the angle $\varphi = 11.8^{\circ}$ which is almost temperature-independent, and with the angle θ equal to 11.2° at 300 K and slowly growing to 12.7° as the temperature drops to 11 K. A more thorough study of the structure of S-Ca₂RuO₄ by the neutron diffraction method at high temperatures done by Friedt et al. [97] showed that the above pattern of distortions with rotations of the octahedrons through angles φ and θ may be augmented by deformations of the octahedrons proper, i.e., the Ru–O distance in the plane monotonically increases with decreasing temperature while the Ru-O distance along the *c* axis monotonically decreases. Near T = 300 K these distances are approximately the same. In other words, the RuO₆ octahedron is prolate along the c axis at T > 300 K, is almost regular at T = 300 K, and becomes more and more oblate as the temperature drops. At T = 90 K the oblateness reaches 2.5%.

The magnetic structure in Ca_2RuO_4 corresponds to the coexistence of two AFM phases depicted in Fig. 14. The A-phase can also be observed in La_2CuO_4 and the B-phase



Figure 13. Diagram of possible structural transitions in Ca_2RuO_4 : (a) initial symmetry group and transitions to possible subgroups; (b) the respective rotations of the RuO_6 octahedrons [86].



Figure 14. Two antiferromagnetic phases of the $S-Ca_2RuO_4$ crystal with the symmetry group *Pbca*. The A-phase dominates [86].

in La₂NiO₄. The A-phase dominates in the stoichiometric S-Ca₂RuO₄ samples. As S-Ca₂RuO₄ is cooled in the temperature range $T_N < T < 150$ K, the susceptibility increases when the field *H* is directed along the hard axes of magnetization [100] and [001] and decreases when the field is directed along the easy axis of magnetization [010], which can be interpreted as development of short-range order with the symmetry of a weak ferromagnet in the RuO₆ layers [98].

The crystal structure of the nonstoichiometric phase O-Ca₂RuO₄ is, at T = 300 K, $P2_1/c$ -symmetric, a situation similar to that for the LTT phase in cuprates. As the temperature is lowered, at $T \approx 200$ K there occurs a first-order phase transition with a wide hysteresis into a *Pbca* structure, just as in S-Ca₂RuO₄. The hysteresis is so wide that even at T = 11 K 24% of the sample remains in the high-temperature $P2_1/c$ phase [86].

The magnetic properties of $O-Ca_2RuO_4$ are characterized by the same A- and B-phases as in S-Ca₂RuO₄ (Fig. 14), but here the B-phase dominates.

The behavior of the electrical properties of S-Ca₂RuO₄ and O-Ca₂RuO₄ is shown in Fig. 15. The dielectric behavior of S-Ca₂RuO₄ above T_N suggests that the dielectric properties cannot be explained by the formation of a two-sublattice AFM structure, since in the SDW state the disintegration of AFM order at $T_{\rm N}$ is accompanied by a metal-insulator transition. Hence, to explain the dielectric properties of S-Ca₂RuO₄ in the paramagnetic phase (the reader will recall that this material is isoelectronic with the metal Sr_2RuO_4), Braden et al. [86] employed the idea of Mott-Hubbard insulator. For O-Ca₂RuO₄, as the temperature decreases and becomes lower than 150 K, a metal-insulator transition takes place. The transition temperature finds itself in the hysteresis region of the structural transformation, so the two transformations could be related. Since short-range order develops in the same region (below 150 K), one cannot exclude the possibility that the three subsystems in the material, the electronic, the structural, and the magnetic, are strongly correlated. Later Fukazawa et al. [89] observed such a metal-insulator transition in stoichiometric Ca₂RuO₄ at $T_{\rm tr} = 357$ K. It appears that the situation with the metal-



Figure 15. Temperature dependence of electrical resistivity in metallic Sr_2RuO_4 , in the Mott-Hubbard insulator S-Ca₂RuO₄, and in O-Ca₂RuO₄, where a metal-insulator transition is evident [86].

insulator transition in Ca_2RuO_4 is similar to that with transitions in vanadium oxides, e.g., in V_2O_3 [92, 99].

3.2 Metal-insulator transitions in Ca_{2-x}Sr_xRuO₄

Recently Nakatsuji and Maeno [100, 101] discovered, in their studies of the quasi-two-dimensional solid solutions $Ca_{2-x}Sr_{x}RuO_{4}$, a complex set of electronic and magnetic transitions from the triplet superconductor Sr₂RuO₄ to the Mott-Hubbard AFM insulator Ca₂RuO₄. For intermediate values of x there are metal–insulator transitions at x < 0.2(Fig. 16) and metallic behavior with short-range AFM order in the interval 0.2 < x < 0.5. At x = 0.5 there is a crossover with the uniform susceptibility $\chi(0)$ rapidly increasing (Fig. 17), which serves as an indication that $Ca_{1.5}Sr_{0.5}RuO_4$ is close to ferromagnetic instability. As $x \rightarrow 2$, the paramagnetic metal transforms into the superconductor Sr₂RuO₄. The region occupied by the superconducting phase is extremely narrow, since triplet pairing is destroyed by defects, as noted in Section 2.4. The phase diagram of $Ca_{2-x}Sr_{x}RuO_{4}$, which shows the various electric and magnetic states, is depicted in Fig. 18. Friedt et al. [97] did a thorough investigation of the structure distortions caused by substitution of Sr for Ca. By applying the neutron diffraction method to powders and single crystals they were able to add structural data to the phase diagram of $Ca_{2-x}Sr_xRuO_4$ (Fig. 19). The figure also



Figure 16. Temperature dependence of electrical resistivity in the *ab* plane for the $Ca_{2-x}Sr_xRuO_4$ system [100].

shows the experimental points of structural phase transitions, T_s , and of magnetic transitions, T_N ; the dashed curve designates the temperature T_P at which the magnetic

susceptibility reaches its maximum (see Fig. 17a). At x < 0.2 the metal-insulator transition is accompanied by a structural transformation in which both phases, the low-temperature and the high-temperature, have the same symmetry group *Pbca* and differ only in the value of parameter *c* (S for 'short *c*' and L for 'long *c*'). In the metallic region there are two structural transitions, which affect the concentration and temperature dependences of the electrical conductivity and magnetic susceptibility.

The entire set of structural transitions can be followed as x decreases, beginning with Sr₂RuO₄ (Fig. 19b) with a K₂NiF₄-type lattice. The rotations of the RuO₆ octahedrons about the c axis by an angle φ lead to the emergence of an $I4_1/acd$ phase. For x = 1.0 the angle $\varphi = 10.8^{\circ}$. Below x = 0.5 there emerge additional rotations by an angle θ about an axis in the *ab* plane, which may lead to a symmetry of a subgroup of the group $I4_1/acd$ or group *Pbca*. At x = 0.2the angle $\theta = 7^{\circ}$; a further decrease in x leads to an increase in θ and oblateness of the octahedrons along the c axis on the transition line from L-*Pbca* to S-*Pbca*, just as in the case for stoichiometric Ca₂RuO₄ described in the previous section.

The temperature dependence of the electrical resistivity of the nonstoichiometric insulator phase with 0 < x < 0.2 is described by a hopping mechanism that allows for SEC effects [equation (24)]. In addition to the transitions into the metallic phase (described in the present section) that are induced by the isoelectronic substitution $Ca^{2+} \rightarrow Sr^{2+}$ and structural distortions, a transition to a metallic state with



Figure 17. Temperature dependence of magnetic susceptibility in the *ab* plane for $Ca_{2-x}Sr_xRuO_4$ with x < 0.5 (a) and x > 0.5 (b). The insets depict the temperature dependence of the reciprocal susceptibility for the same compositions [101].



Figure 18. Electronic and magnetic phase diagram of $Ca_{2-x}Sr_xRuO_4$. The following notation has been used: P for paramagnet, CAF for canted antiferromagnet, M for magnetic phase, SC for superconducting phase, Me for metal, I for insulator, and $T_{M/NM}$ for the metal–nonmetal transition point [100].



Figure 19. Diagram of structural phase transitions in $Ca_{2-x}Sr_xRuO_4$ (a), and various types of octahedron rotation in the respective phases (b) [97].

doping is also possible. Such a transition was studied using the alloy series of $Ca_{2-x}La_xCuO_4$ single crystals (0 < x < 0.2) in which the substitution $Ca^{2+} \rightarrow La^{3+}$ leads to electron doping [102]. Actually, this means that a third dimension, the carrier concentration, is added to the two-dimensional diagram of Fig. 18, so that a three-dimensional phase diagram emerges. According to Fukazawa and Maeno [102], the metallic phase in $Ca_{2-x}La_xRuO_4$ resembles, in thermodynamic and transport properties, the metallic phase of $Ca_{2-x}Sr_xRuO_4$ with x > 0.5, in which the spin fluctuations are of the ferromagnetic type. The opposite type of doping, hole doping, is achieved in samples with an excess of oxygen, $Ca_2RuO_{4+\delta}$.

Fang and Terakura [103] attempted to explain the magnetic phase diagram of Ca_{2-x}Sr_xRuO₄ on the basis of first-principles band-structure calculations in the LDA approximation. They found that the octahedron rotations by an angle φ about the c axis stabilize the FM state since such rotations substantially reduce the p-d- π hybridization of the Ru d_{xy} orbital with the 2p orbitals of the in-plane oxygen O1. This leads to a reduction of the width of the γ -band, so that the Fermi level moves closer to the Van Hove singularity, and this simplifies guaranteeing Stoner's criterion. As for the α and β -bands, the state of the d_{yz} and d_{zx} orbitals changes little under rotations about the c axis. The introduction of rotations about an axis in the *ab* plane reduces the widths of all three t_{2g} bands, which enhances the nesting effect and stabilizes the AFM phase. The results of Fang and Terakura [103] are at first glance appealing. Two remarks concerning these results are in order, however.

1. The rutheno-cuprate RuSr₂GdCu₂O₈ has exactly the same rotations of RuO₆ octahedrons about the *c* axis as the Ca_{2-x}Sr_xRuO₄ system, with even the rotation angle $\varphi \approx 14^{\circ}$ being close to the value of φ for Ca_{2-x}Sr_xRuO₄ [93]. Nevertheless, RuSr₂GdCu₂O₈ has no FM order — only AFM order (see Section 6).

2. Just as all LDA calculations, those done by Fang and Terakura [103] are unable to describe the Mott-Hubbard insulator at finite temperatures. The most that such calculations can achieve is to produce an antiferromagnetic dielectric ground state (the SDW state) that must transform into a metallic state as the temperature becomes higher than T_N . Actually, Ca₂RuO₄ remains an insulator even above T_N . To describe a Mott-Hubbard insulator one must take SEC effects into account in the band structure calculations.

Recently Anisimov et al. [104] calculated the electronic structure and magnetic properties of Ca_{2-x}Sr_xRuO₄ with allowance for SEC effects by the LDA + U and LDA ++ methods (see Section 2.2). The density of states for Sr₂RuO₄ is shown for different values of the correlation energy U in Fig. 20. At U = 1.5 eV, the α , β -band splits into the lower and upper Hubbard bands and the $d_{yz, zx}$ electrons become localized. At U = 2.5 eV, the d_{xy} states also become localized. In their calculations the researchers assumed that SEC effects are more strongly expressed for the α , β -band, since according to the results of LDA calculations for Sr₂RuO₄ this band is twice as narrow as the γ -band. According to Ref. [104], when 0.5 < x < 2.0 and 0.2 < x < 0.5, the occupancy of the bands $(\alpha\beta, \gamma)$ can be written as (3,1), i.e., three electrons in the α , β -band and one in γ , while when 0 < x < 0.2, the occupancy is (2,2), i.e., the γ -band is completely occupied, and the number of holes is zero, $n_{\gamma}^{h} = 0$. This conclusion contradicts the results of Mizokawa et al. [105], who in their experiments on X-ray O1s absorption spectra in Ca2RuO4 found that $n_{\gamma}^{\rm h}/n_{\alpha\beta}^{\rm h}$ is equal to 1 at T = 300 K and to (1/2)/(3/2)at T = 90 K. Furthermore, to explain the localization of one hole in the α , β -band in the (3,1) configuration, Anisimov et al. [104] are forced to assume that there is additional orbital ordering of the antiferromagnetic type, which is not observed



Figure 20. Results of calculations of the density of states for Sr_2RuO_4 by the LDA + DMFT method at different values of parameter U. Solid curves represent the partial contribution of the d_{yz} and d_{zx} orbitals and the dashed curves, the contribution of d_{xy} orbitals [104]. \

in experiments. The reason for the discrepancy with the experimental results probably lies in the fact that from the different ways of solving the problem Anisimov et al. [104] did not select the optimal one.¹

A different version of the band structure of the ruthenates $Ca_{2-x}Sr_xRuO_4$ has been proposed in Ref. [106] and also allows for SEC effects (Fig. 21). It assumes that the α , β -bands are split into Hubbard subbands in Sr₂RuO₄ but that the γ -band is not split, although it is close to the Mott–Hubbard transition point. In one-electron band theory, the α - and β -bands are almost perfectly degenerate: the splitting caused by interband hybridization t_{\perp} is small, $t_{\perp} \sim 0.1$ eV. The splitting increases because of interband Coulomb interaction. Indeed, in the mean-field approximation,

$$V_{\alpha\beta} n_{\alpha} n_{\beta} = V_{\alpha\beta} \langle n_{\alpha} \rangle n_{\beta} + V_{\alpha\beta} n_{\alpha} \langle n_{\beta} \rangle$$
(26)

the band energies are renormalized,

$$egin{aligned} & arepsilon_lpha o \widetilde{arepsilon}_lpha = arepsilon_lpha + V_{lphaeta} \left\langle n_eta
ight
angle \,, \ & arepsilon_eta o \widetilde{arepsilon}_eta = arepsilon_eta + V_{lphaeta} \left\langle n_lpha
ight
angle \,, \end{aligned}$$

and the splitting of the α , β -bands is

$$\Delta \varepsilon = \tilde{\varepsilon}_{\beta} - \tilde{\varepsilon}_{\alpha} = \varepsilon_{\beta} - \varepsilon_{\alpha} + V_{\alpha\beta} (\langle n_{\alpha} \rangle - \langle n_{\beta} \rangle) \sim t_{\alpha\beta} + \frac{2}{3} V_{\alpha\beta} .$$
(27)

Here I have used the data on the occupancy of the α , β -bands from Singh's calculation [12]. At $V_{\alpha\beta} \sim 1$ eV the splitting $\Delta \varepsilon \approx 0.7 - 0.8$ eV, which is comparable with the band width $W_{\alpha} = W_{\beta} = 1.5$ eV. As in band structure calculations, there are two electron Fermi surfaces in Sr₂RuO₄, which are formed by the γ -band and the upper Hubbard β band (β -UHB), and a single hole α -band with a hole concentration $n_{\gamma}^{h} \approx 0.3$ Å⁻³. Since the number of holes in the α -band is small, the spectral weight of α -LHB is also small ($\sim n_{\gamma}^{h}/2$), so the Mott– Hubbard splitting does not manifest itself in the almost completely occupied α -band [41, 42].

The width of the γ -band decreases and the system approaches the critical point $U \sim U_c$ due to rotations of the octahedrons about the *c* axis (Fig. 21b). Since such rotations do not affect the α , β -bands [103], the α , β -bands in the interval 0.5 < x < 2.0 are assumed to be weakly dependent on *x*. Further diminishing of *x* and the related rotations through angles φ and θ decrease the widths of all bands, so that at x = 0 the γ -band is split and Mott–Hubbard gaps between the filled γ -LHB and the empty γ -UHB and between the filled β -LHB and the empty β -UHB are formed. According to Ref. [106], for Ca₂RuO₄ the α -band is completely occupied.

In this picture of the band structure evolution beginning with metallic Sr₂RuO₄, the hole ratio $n_{\gamma}^{h}/n_{\alpha\beta}^{h} = 1$, in accordance with XAS data [105]. As the temperature of Ca₂RuO₄ becomes lower, the octahedrons become oblate, which in terms of one-electron orbitals means that the degeneracy of their orbitals is lifted, and this makes the energy of *yz/zx* orbitals higher than that of *xy* orbitals. However, when the Coulomb interaction was taken into account in the Hartree– Fock approximation, it was found that at T = 90 K (in the oblate octahedron) the two holes fill the *yz* and $(xy + izx)/\sqrt{2}$ orbitals, so that $n_{\gamma}^{h}/n_{\alpha\beta}^{h} = (1/2)/(3/2)$, in accordance with O1s-XAS [105].

The competition between the FM and AFM fluctuations in ruthenates has been discussed in Section 2 in band-theory terms. Let us study this problem from the viewpoint of the opposite SEC limit. As is known, in the Hubbard model with one electron per atom for the alternative lattice the AFM state is stable for all values of U/W. However, in the limit $U = \infty$ only one carrier is needed to stabilize the Nagaoka FM state. In the SEC regime where $U \gg W$, virtual transitions between LHB and UHB lead to the AFM exchange $J = 4t^2/U$, while intraband motion ensures the FM exchange of the kinematic type, $I \sim t$. Let x be the carrier concentration near half-filling of the band, i.e., $n_e = 1 + x$ for $n_e > 1$ (electron doping) and $n_{\rm e} = 1 - x$ for $n_{\rm e} < 1$ (hole doping). One can then make a qualitative estimate of the competition between FM and AFM fluctuations in the SEC regime: the gain from FM ordering per bond is $E_{\rm FM} \sim Ix$, while the gain from AFM ordering per bond is $E_{\text{AFM}} \sim J(1-x^2) \sim (4t/gz)(1-x^2)$, where z is the number of nearest neighbors, W = zt, g = U/W, and the factor $(1 - x^2) = n_e(2 - n_e)$ guarantees the absence of AFM fluctuations in an empty band and in a filled band. Comparing E_{FM} and E_{AFM} , we see that for $x < x_{\text{c}}$ the AFM state is preferable, while for $x > x_c$ the FM phase is stabilized. Here

$$x_{\rm c} = \sqrt{\left(\frac{gz}{8}\right)^2 + 1} - \frac{gz}{8}.$$
 (28)

In the limit $U \to \infty$, $x_c = 4/gz \to 0$ in accordance with Nagaoka's theorem. The simple estimate (28) is corroborated by a calculation of T_N in the generalized random phase

¹ This remark was made by A Lichtenstein to whom I am grateful for a discussion of the problems of electronic structure calculations with allowance for SEC effects.



Figure 21. Three-band model of the electronic structure of ruthenates with allowance for strong SEC effects [106]. Here UHB and LHB stand for upper and lower Hubbard bands. The cases (a), (b), and (c) correspond to Sr_2RuO_4 , $Ca_{1.5}Sr_{0.5}RuO_4$, and Ca_2RuO_4 .

approximation [107], where for small values of x

$$T_{\rm N}(x) = \frac{1}{2} zJ - \frac{1}{4} xzt.$$
⁽²⁹⁾

Here the second term on the right-hand side describes the suppression of AFM fluctuations caused by kinematic exchange.

Let us now describe the competition between the FM and AFM fluctuations in ruthenates in terms of the band structure in the SEC regime (Fig. 21). For Sr_2RuO_4 , the γ band is on the metallic side of the Mott transition. According to band theory, a strong FM interaction with a Stoner factor $IN(\varepsilon_{\rm F}) \ge 1$ provides strong FM fluctuations. At the same time, interband transitions between Hubbard α and β -subbands in the SEC regime produce strong AFM fluctuations in the same way that within the band approach, nesting for the Fermi surface of the α , β -bands produces AFM fluctuations. In Sr₂RuO₄, according to Mazin and Singh's LDA calculations [22], $J \sim I$. In the SEC regime, the FM exchange $I \sim t_{\gamma}$, while the AFM exchange $J = 4t_{\alpha\beta}^2/U \approx$ t_{γ}^2/U , and for $t \ll U$ the FM exchange is predominant. Near the Mott transition $U \sim zt_{\gamma}$, which means that $J/I \sim$ $t_{\gamma}/U \sim 1/z = 1/4$ in the two-dimensional RuO₂ layer. In the effective low-energy model for Sr₂RuO₄, as the above analysis suggests, one must retain the hoppings of carriers in the Hubbard band, AFM exchange J, and FM exchange I, i.e., one ends up with the t-J-I model proposed in Ref. [108] and discussed in Section 2.6. Neither the LDA approximation nor the SEC limit operate at the Mott transition point, but the above estimates show that the two opposite limiting cases suggest that in ruthenates J and I are of the same order of magnitude.

As the band structure in Fig. 21a is replaced with that in Fig. 21b, i.e., x in the $Ca_{2-x}Sr_xRuO_4$ system decreases, the AFM exchange in α , β -bands remains almost the same, while the binding energy of the FM phase decreases, since the carrier concentration at the bottom of γ -UHB becomes lower and an additional AFM exchange caused by virtual interband γ -LHB $\leftrightarrow \gamma$ -UHB transitions comes into play. Both factors lead to gradual predominance of AFM fluctuations below x < 0.5. Note that in the concentration range of Fig. 21b the γ -electrons are still not localized and the localized moment is formed chiefly by the almost comple-

tely filled β -LHB, with the result that an effective spin is close to S = 1/2. This situation was observed by Nakatsuji and Maeno [101] in their susceptibility measurements.

4. Spin fluctuation effects in the conducting ruthenates (Sr/Ca)RuO₃ and (Sr/Ca)₃Ru₂O₇

Among all the known oxides of 4d elements, $SrRuO_3$ is the only FM metal (Curie temperature $T_M = 165$ K and magnetization $\mu = 1.6\mu_B/Ru$) that has a distorted cubic perovskite structure [17–21]. Spin–orbit coupling in 4d elements is stronger than in 3d-metal compounds, which means that one can expect a higher degree of magnetic anisotropy and the presence of magnetooptical properties. Indeed, measurements of the exchange magnetization of polycrystalline [109] and single-crystal [21] samples of $SrRuO_3$ show that saturation of M(H) is not reached even in fields higher than 1 T. Strong magnetooptical effects were detected by Klein et al. [110] in thin $SrRuO_3$ films.

Band structure calculations [111-113, 16] have reproduced the main features of magnetic properties. According to the results of specific-heat and photoemission-spectrum measurements [112, 114], the density of states and band widths differ from the results of band calculations, which is typical of SEC effects. Studies of the transport properties of SrRuO₃ [112, 115–117] have shown a non-Fermi-liquid temperature behavior, which fits the phenomenological definition of a 'poor' metal [118]. Measurements of reflectance in SrRuO₃ films [119] showed that the low-frequency conductivity $\sigma_1(\omega) \sim 1/\omega^{1/2}$, in contrast to $\sigma_1(\omega) \sim 1/\omega^2$ observed in typical metals. Note that the dependence $\sigma_1(\omega) \sim 1/\omega^{1/2}$ is also observed in HTSC cuprates [120]. Mazin and Singh [16] provided a qualitative explanation of the unusual transport properties of SrRuO₃ on the basis of LDA calculations. They stressed the importance of the strong electron-phonon and electron-magnon interactions and of the complex structure of the Fermi surfaces in both spin subbands, consisting of electron, hole, and open surfaces. Above $T_{\rm M}$ there is also strong electron scattering by paramagnetic spin fluctuations. According to Mazin and Singh [16], in SrRuO₃ there is a strong magnetoelastic interaction, whereby it is difficult to separate the contributions of electron-phonon and electron-magnon interactions.

The isostructural and isoelectronic substitution $Sr \rightarrow Ca$ suppresses the FM order. The crystal structure of SrRuO₃ and CaRuO₃ of the GdFeO₃ type (the symmetry group Pbnm) coincides with the structure of another known group of oxides, manganites LaMnO₃. As in the system $Ca_{2-x}Sr_{x}RuO_{4}$, the difference in the ionic radii of Ca^{2+} and Sr^{2+} leads to a situation in which the octahedron rotation angles in CaRuO₃ are twice as large as those in SrRuO₃. CaRuO₃ is a paramagnetic metal over the entire temperature range. The band structure calculations of the total energy as a function of magnetization done by Mazin and Singh [16] for CaRuO₃ revealed the presence of an extremely wide flat section extending up to $\mu = 1.5\mu_{\rm B}/{\rm Ru}$. A similar flat section is known to exist in fcc palladium. Hence even light doping can stabilize the FM state. A 2% substitution of Ti for Ru in CaRuO₃ is sufficient for stabilizing the FM state [121]. Moreover, paramagnetic spin excitations in CaRuO₃ should have extremely low frequencies, and magnetic impurities may induce giant local moments.

To establish the relationship between the FM state and rotations of octahedrons, Mazin and Singh [16] also calculated the energy and magnetization of CaRuO₃ for different rotation angles φ . The calculation for an angle φ corresponding to CaRuO₃ yielded $\mu = 1.68\mu_B/Ru$ and a gain of $\Delta E = 0.06 \text{ eV/Ru}$ in the energy of the FM state, which is very close to the results for SrRuO₃. The calculation for an angle φ averaged over SrRuO₃ and CaRuO₃ produced $\mu = 1.53 \mu_{\rm B}/{\rm Ru}$ and $\Delta E = 0.029 \ {\rm eV}/{\rm Ru}$. According to Ref. [16], $\Delta E = 0$ corresponds exactly to the value for the experimental structure of CaRuO3. These calculations exposed the reason for the strong magnetoelastic interaction in the system $Ca_{1-x}Sr_xRuO_3$. The isoelectronic oxide BaRuO₃ has several modifications of the crystal lattice of the hexagonal-perovskite type, and none of them has magnetic order [122].

The two-layered ruthenate $Sr_3Ru_2O_7$ has aroused much interest as a candidate for a substance exhibiting superconductivity of the triplet type by analogy with Sr_2RuO_4 . Indeed, the two coupled RuO_2 layers possess a higher structural stability than the single layer in Sr_2RuO_4 . Since the electronic structure is quasi-two-dimensional, one can expect that the basic features of the electronic structure of Sr_2RuO_4 will be repeated in the two-layered ruthenate with a splitting common for the two-layer case, which Hase and Nishihara [123] and Singh and Mazin [124] showed to be the case by their band calculations. Since triplet superconductivity is extremely sensitive to the presence of defects, the crystals used in experiments must be of high quality.

Although polycrystalline samples of Sr₃Ru₂O₇ were synthesized long ago by several research groups [125–127], the study of their electrical and magnetic properties has begun only recently. Different researchers report different results, which is probably due to the difference in sample quality. No one has discovered superconductivity in these samples. The conclusion about the AFM ground state with localized moments was drawn by Cava et al. [128] on the basis of an analysis of the temperature dependence of the magnetic susceptibility, $\chi(T)$, for polycrystals, a dependence that obeys the Curie – Weiss law with a maximum of $\chi(T)$ at 20 K and $\theta_{\rm N} < 0$. At roughly the same time, the first measurements involving single crystals grown by the self-flux technique from SrCl₂ in Pt crucibles attested to weak itinerant ferromagnetism [129]. Recently, a research group from Kyoto used the crucibleless floating-zone method to grow perfect single crystals in which the residual resistivity in the *ab* plane was $\rho_{\rm res} \approx 3-4 \,\mu\Omega$ cm [130]. Later the same group produced single crystals with $\rho_{\rm res} \approx 2 \,\mu\Omega$ cm [131]. Nevertheless, none of these crystals was found to exhibit superconductivity at T > 50 mK. Figure 7 clearly shows that in Sr₂RuO₄ triplet superconductivity is completely destroyed by defects at $\rho_{\rm res} > 1 \,\mu\Omega$ cm. Hence one can expect that further progress in growing high-quality Sr₃Ru₂O₇ crystals will make it possible to detect triplet superconductivity.

Magnetic measurements involving the Kyoto singlecrystal samples revealed the presence of a susceptibility peak at $T^* = 16$ K [132]. A similar peak in the temperature dependence of the Hall coefficient, $R_H(T)$, was discovered in another series of Sr₃Ru₂O₇ single crystals [133]. Different authors give a different interpretation of the maximum at point T^* . According to Lui et al. [133], AFM fluctuations are predominant below T^* , while FM fluctuations are predominant above T^* . AFM spin fluctuations have indeed been identified by inelastic neutron scattering at T = 1.5 K [134]. At the same time, elastic neutron scattering does not reveal the presence of long-range magnetic order in weak external fields [135].

In the case of strong magnetic fields, Perry et al. [131] and Grigera et al. [136] discovered a metamagnetic transition (Fig. 22), which manifested itself in the field dependences of the magnetization, M(B), and magnetoresistance, $\rho(B)$. Figure 22 shows that the critical fields are different: $B_{\rm c}(||ab) = 5.5$ T and $B_{\rm c}(||c) = 7.7$ T. Metamagnetism can



Figure 22. Field dependences of magnetization (a) and magnetoresistance (b) in $Sr_3Ru_2O_7$ single crystals for different configurations of the magnetic field *B* [131].

be observed at temperatures below 10 K. Here, the very term metamagnetism requires explaining. Usually this term, originating with Néel [137], is used in describing the collapse of sublattices in antiferromagnets in which the anisotropy field $H_{\rm A}$ is higher than the exchange field $H_{\rm E}$ (e.g., see Ref. [138]). In this case there is no intermediate phase with canted sublattices, and an antiferromagnet in a weak field becomes a ferromagnet in a strong field. In the case of Sr₃Ru₂O₇ there is no antiferromagnetism in weak fields. Furthermore, here we are dealing with metamagnetism in a system of itinerant electrons. Nevertheless, the discovery of metamagnetism is a clear indication of the presence of strong FM interactions in Sr₃Ru₂O₇. Incidentally, metamagnetism in Sr₂RuO₄ has not been discovered in fields as high as 33 T [139]. Other examples of conducting metamagnets are MnSi [140] and CeRu₂Si₂ [141]. The importance of the discovery of FM ordering in Sr₃Ru₂O₇ in strong fields amounts not only to revealing the interesting properties of this metal but also to the fact that this is the first macroscopic corroboration of the presence of FM interactions in quasi-two-dimensional RuO₂ layers, whose role was thoroughly discussed in Section 2.

Perry et al. [131] and Grigera et al. [136] also discussed the question of whether the metamagnetic transition they discovered in $Sr_3Ru_2O_7$ is a true phase transition in the field or a crossover and conclude that in both scenarios low-temperature critical points may exist. But is there any experimental evidence of the existence of critical fluctuations related to metamagnetism in $Sr_3Ru_2O_7$? Such evidence may be obtained by analyzing the temperature dependences of electrical resistivity $\rho(T)$ and specific heat (Fig. 23). The power-law



Figure 23. Manifestations of critical quantum fluctuations in Sr₃Ru₂O₇ in the vicinity of a metamagnetic transition in the temperature dependences of resistivity $\rho(T) = T^{\alpha}$ (a) and specific heat (b). Figure 22a depicts the dependence of the exponent α on temperature and field for B||I||ab, and Fig. 22b for B||c.

dependence $\rho(T) = T^{\alpha}$ is reduced to a Fermi-liquid dependence with $\alpha = 2$ only at T < 15 K and far from the metamagnetic transition, for $B < B_c$ and $B > B_c$. At $B \sim B_c$ and for all values of T(T > 2.5 K in the experiment of Perry et al. [131]) there is a non-Fermi-liquid dependence with $1 < \alpha < 1.25$. Note that the non-Fermi-liquid behavior $\rho(T) \sim T^{1.2}$ is known to exist for CePd₂Si₂ within a broad temperature range.

The electronic specific heat $C_{\rm el}/T$ described by formula (25) in the case of a Fermi liquid, in a zero field first increases with decreasing T, but then, after it reaches its maximum at 7 K, it follows a dependence close to that described by formula (25). In a finite magnetic field, $C_{\rm el}/T$ monotonically increases with decreasing T, and in a field $B = B_c$ (note that the fields in Figs 23a and b are oriented differently, with the result that the critical values differ) $C_{\rm el}/T \sim \lg T$. As we move farther from the critical point, at B = 9 T the slope diminishes. Thus, both thermodynamic and transport properties indicate that there are critical fluctuations determining the non-Fermi-liquid behavior of Sr₃Ru₂O₇ near a quantum critical point. Perry et al. [131] give an interesting physical interpretation of these fluctuations. The magnetic moment appears in an itinerant ferromagnet as a result of spontaneous separation of the Fermi surfaces with spins up and down. In a band metamagnet, when the field is higher than B_c an additional magnetic moment appears for the same reason. Then the critical fluctuations just discussed can be considered fluctuations of size and form of the Fermi surfaces. Although these fluctuations have a wave vector q = 0, nevertheless, in a quasi-two-dimensional system the polarized and unpolarized Fermi surfaces will exhibit different nesting properties, so that one can expect critical fluctuations with q = 0 to be related to fluctuations with large $q \sim \pi/a$.

The magnetic measurements of Cao et al. [88] revealed that for x > 1/3 there is AFM ordering in the $(Ca_xSr_{1-x})_3Ru_2O_7$ system. The electronic structure of $Ca_3Ru_2O_7$ and the ARPES measurements allowed Puchkov et al. [142] to classify this material as a 'poor' metal in which the spectral weight near the Fermi level is suppressed (but not completely) by SEC effects.

5. Magnetism in the double perovskite Sr₂YRuO₆

Actually, the crystal structure of the double perovskite Sr₂YRuO₆ coincides with that of SrRuO₃ in which every second Ru ion is replaced with a Y ion. This is an AFM insulator with $T_{\rm N} = 26$ K. The ruthenium ion is pentavalent, Ru⁵⁺, with a $4d^3$ configuration in the high-spin ${}^4A_{2g}$ state with spin S = 3/2, The family of isostructural double perovskites $M_2^{2+}X^{3+}$ Ru⁵⁺O₆ (M = Ca, Sr, Ba and X = La, Y) has been synthesized in the form of polycrystals whose magnetic properties have been studied by the neutron diffraction method [4]. In double perovskites, the structural units are RuO₆ and YO₆ octahedrons, and as a result of octahedron rotations the symmetry is lowered to P21/n. Since both Y³⁺ and Sr²⁺ are fully ionized, one can expect that they play no active role in the formation of the electrical and magnetic properties of double perovskites. From this viewpoint, Sr₂YRuO₆ can be considered as a system of $(RuO_6)^{7-}$ clusters not bound directly and ordered into a slightly distorted fcc lattice. The binding of two neighboring ruthenium ions is achieved via two neighboring oxygen ions, i.e., Ru-O-O-Ru. According to neutron



Figure 24. Antiferromagnetic order of the first type in Sr₂YRuO₆; only the ruthenium ions forming an fcc lattice are shown [4].

diffraction data [4], the fcc lattice of ruthenium has AFM order of the first type (Fig. 24) with a magnetic moment $\mu = 1.85\mu_{\rm B}$ instead of the nominal value of $3\mu_{\rm B}$ for S = 3/2.

The magnetic measurements done by Cao et al. [143] that involved Sr_2YRuO_6 single crystals have proved that below T_N a weak ferromagnetic state, rather than a true AFM state, is realized, i.e., the sublattices are canted. This follows from the absence of anisotropy in $\chi(T)$ below T_N (in an antiferromagnet the $\chi(T)$ along the easy and hard axes of magnetization are different) and from the presence of a hysteresis loop in the magnetization curve M(H). The remanent magnetization in H = 0 at T = 5 K is $0.05\mu_{\rm B}/{\rm Ru}$ and tends to zero as $T \rightarrow T_{\rm N}$. In a strong magnetic field (H = 7 T), $M = 0.5 \mu_{\rm B}/{\rm Ru}$, which amounts to only one-sixth of the expected saturation magnetization for S = 3/2. No singularities in the M(H) curves of the metamagnetic transition type has been discovered in $Sr_3Ru_2O_7$ up to H = 7 T. The shape of the M(H) dependence changes very little as T increases up to 70 K, which suggests that there are strong spin fluctuations above T_N .

Measurements of the temperature dependences of the electrical resistivity and magnetoresistance involving the same Sr₂YRuO₆ single crystals revealed the presence of singularities near $T_{\rm N}$ [143]. There is no reason to believe that each kink in the curves represents a new phase transition, so that the validity of the conclusion drawn by Cao et al. [143] about a Mott transition at 17 K is doubtful. I believe that both in $\rho(T)$ and $\Delta \rho_{\rm H}(T)$ a peak near $T_{\rm N}$ exists and that this peak indicates the presence of strong carrier scattering by spin fluctuations, while there is also the smooth section in the curves that is typical of a semiconductor. In the 80–150-K range the dependence $\rho_{ab}(T)$ exhibits activation behavior with a gap $E_{\rm g} = 76$ meV [143], which is close to Mazin and Singh's calculations [16], $E_{\rm g} = 80$ meV.

Mazin and Singh [16] used in their band structure calculations the linear augmented plane wave (LAPW) method for the AFM and FM phases. The energy of the AFM phase is only 0.095-eV/Ru lower than that of the FM phase, which suggests that in this ruthenate, just as in other ruthenates, there is competition between FM and AFM interactions. The electronic structure of Sr_2YRuO_6 in the AFM phase corresponds to a semiconductor with a gap $E_g = 0.08$ eV due to the spin splitting of hybridized

 $t_{2g}(Ru) - p(O)$ states. For the FM phase, the spin subbands overlap and form a semimetallic state.

Due to the fact that the neighboring RuO_6 octahedrons in Sr_2YRuO_6 have no common oxygen ions and are separated by an additional O–O bond, the electronic structure is approximated fairly well in the tight-binding method [16]. The magnetic properties can be described by the effective Heisenberg Hamiltonian

$$H_{\rm H} = -\frac{1}{2} \sum_{fR} J(R) \mathbf{S}_f \cdot \mathbf{S}_{f+R} \,, \tag{30}$$

where J(R) is the effective exchange integral. According to Mazin and Singh's calculations [16], for the nearest neighbors of the Ru ion in the fcc lattice 2J = 0.05 eV. In view of the indirect nature of the exchange interaction via chains of several atoms, the exchange interaction between next-nearest neighbors, *I*, is much smaller than *J*. This research points to the discrepancy between the large value of *J* for which one can expect that $T_N \sim 700-900$ K, and the small value of $T_N = 26$ K in Sr₂YRuO₆.

What makes the magnetic state with the AFM interaction of the nearest neighbors in the fcc lattice so special is that, in contrast to simple cubic and bcc lattices, in an fcc lattice it is impossible to align all spin of the nearest neighbors antiparallel to the given spin, for all sites of the lattice. In other words, it is impossible to divide the lattice into two interpenetrating ferromagnetic sublattices. There are always spin pairs for which AFM bond is disadvantageous. Such bonds are said to be frustrated. Lately there has been an upsurge of interest not only in the magnetic properties of frustrated systems but also in their electronic properties. Among possible examples may be the observation of the unusual behavior of heavy fermions in LiV2O4 [144, 145] and the discovery of superconductivity with $T_c = 1$ K in Cd₂Re₂O₇ [146]. For classical spins in the Hamiltonian (30) for frustrated lattices, the two-sublattice AFM state is not the ground state; for instance, for an fcc lattice one can build a more advantageous state with eight sublattices (see Gekht's review [147]).

The situation with quantum spin systems is even more complicated. Frustrations suppress the two-sublattice AFM state, with the state of a quantum spin liquid stabilized instead [148, 149]. The reason for the suppression of the AFM state is the presence of very strong spin fluctuations. For an AFM state of the first type (Fig. 24), the mechanism of suppression of this state and the nature of the quantum spin liquid have been thoroughly studied by Kuz'min [150]. Due to frustration, the exchange interactions in the *ab* plane contribute nothing to the magnon dispersion law which becomes onedimensional in the vicinity of the particular points of the Brillouin zone, $\Gamma = (0,0,0)$, $Z = (0,0,2\pi)$, and others. As a result, the spin-wave renormalizations diverge for $\langle S^z \rangle$ logarithmically and for T_N in a power-law manner, thus destroying the AFM state. To stabilize this state one must allow for additional small corrections to the exchange J: the exchange interaction between next-nearest neighbors or the anisotropy of the exchange or a single-ion type or the anisotropic Dzyaloshinskii exchange; each of these corrections can truncate the spin-wave divergences and stabilize the AFM phase observed in Sr₂YRuO₆. A discussion of frustration effects [16] in terms of the Ising model, where there are no spin waves, is not enough for understanding the discrepancy between the small values of $T_{\rm N}$ and the large values of J.

6. Coexistence of superconductivity and magnetism in rutheno-cuprates

These materials are the link between the world of HTSC cuprates and the world of ruthenates. Two families of layered rutheno-cuprates are known: RuSr₂LCu₂O₈ (the Ru-1212 structure), and $RuSr_2L_{1+x}Ce_{1-x}Cu_2O_{10}$ (the Ru-1222 structure), with L = Sm, Eu, and Gd. The first polycrystalline samples of Ru-1212 were synthesized by Bauerfeind et al. [151] and Felner et al. [152] and consisted of alternating doublelayer CuO₂ and monolayer RuO₂. The observation of superconductivity below $T_c = 16$ K and ferromagnetism below $T_{\text{Curie}} = 133 \text{ K}$ in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ by Bernhard et al. [153] (Fig. 25) immediately revived interest in the longstanding problem of coexistence of superconductivity and ferromagnetism [154]. It must also be noted that one of the first observations of the coexistence of superconductivity and ferromagnetism involved ruthenium alloys, precisely $Ce_{1-x}Gd_xRu_2$ [155]. According to Bernhard et al. [153], FM order sets in RuO₂ layers with a magnetic moment $\mu(\mathbf{Ru}) = 1\mu_{\mathbf{R}}$, while superconductivity is related to CuO₂ layers, with the spatial separation of layers preventing the superconducting state from being destroyed by the strong internal magnetic field of the FM layer. The conclusion concerning FM ordering of the RuO₂ layer was drawn on the basis of observations of the hysteresis loop in the magnetiza-



Figure 25. Temperature dependences of magnetic susceptibility (a) and magnetization (b) in a polycrystalline sample of RuSr₂GdCu₂O₈ taken on cooling in different magnetic fields; their behavior points to the coexistence of ferromagnetism and superconductivity [153].

tion curves and of the results of muon spin resonance (μ SR) measurements. Later, variations in the composition of the Ru_{1-x}Sr₂LCu_{2+x}O₈ system made it possible to raise T_c to $T_c^{max} = 72$ K for x = 0.3-0.4 [156].

The first-principles calculations of the band structure of Ru-1212 conducted by Pickett et al. [157] clarified the question of why magnetism does not suppress superconductivity. First, the large magnetic moment of Gd^{3+} , $\mu(Gd) = 7\mu_{\rm B}$, was found to have no effect on the electronic structure of the CuO₂ and RuO₂ layers due to the small overlap of the respective wave functions. Second, the electronic structure of the CuO₂ layer is almost independent of the magnetic state of RuO_2 . Despite the strong exchange splitting ($\sim 1 \text{eV}$) of the spin subbands in the RuO₂ layer, the exchange splitting induced in the CuO₂ layer is small (about 25 meV) due to the specific nature of the small overlap of the wave functions of the nearly two-dimensional electronic structures of the CuO₂ and RuO₂ layers. Hence to the first approximation the electronic structures of the CuO₂ and RuO₂ layers can be considered independent, and their relationship is materialized through their common chemical potential.

The way in which SEC effects influence the electronic structure of cuprates and ruthenates is known and was discussed in Section 2.6. There the magnetic mechanisms of pairing in cuprates and in Sr₂RuO₄ were compared within the framework of the t-J-I model. Since rutheno-cuprates have the same CuO₂ and RuO₂ layers with strongly correlated electrons and there is competition between ferromagnetic and antiferromagnetic interactions, it is only natural to attempt to describe the coexistence of ferromagnetism in the RuO₂ layer and superconductivity in the CuO₂ layer by using the t-J-Imodel. When this model is applied to Ru-1212, it is assumed that both types of layers are described by the same Hamiltonian (18) which, however, has different sets of parameters: $J_{Cu} \gg I_{Cu}$ for the CuO₂ layer and $J_{Ru} \leqslant I_{Ru}$ for the RuO_2 layer, while the hopping parameters are roughly equal, $t_{Cu} \sim t_{Ru} \sim 0.1$ eV. In the CuO₂ layer the current carriers are the holes close to the top of the lower Hubbard subband of the $d_{x^2-y^2}-p = \sigma$ band, while in the RuO₂ layer these carriers are the electrons near the bottom of the upper Hubbard subband of the $d_{xy} - p = \pi$ band (the γ -band); the α , β -bands of the RuO₂ layer act as a reservoir for the particles. On the whole, the electronic structure of Ru-1212 is considered in Ref. [158] as being the electronic structure of the CuO₂/SrO/RuO₂ superlattice.

Due to AFM spin fluctuation, the CuO₂ layer exhibits superconductivity of the singlet type with $d_{x^2-v^2}$ symmetry. In the RuO_2 layer there is severe competition between triplet superconductivity and FM and AFM fluctuations, so that the main question within such an approach is: Why does the same RuO₂ layer in Sr₂RuO₄ become superconducting, while in Ru-1212 it is magnetically ordered? To answer this question, in Ref. [158] the phase diagram of the t-J-I model was examined in the $(J = 0, I/t, \text{ carrier concentration } n_0)$ plane. In this diagram there are phases of a normal metal, a triplet superconductor, and a ferromagnet, with Sr₂RuO₄ placed in the superconducting region close to the boundary of the transition to the FM phase. A slight decrease in carrier concentration stabilizes the FM state. In Ru-1212 this decrease is related to the electron transfer from the CuO₂ layer to the RuO₂ layer.

The charge state of copper and ruthenium was discussed on the basis of an analysis of the relationship between

$$Y^{3+}Ba_2^{2+}Cu_2^{2.2+}Cu^{2.6+}O_7^{2-}, (31)$$

and, generally, the copper in the CuO₂ layer is in the Cu^{2+*p*} state, with p = 0.05 - 0.25, where *p* is the hole concentration per CuO₂ layer, for Ru-1212 the corresponding formula can be written as follows:

$$\mathrm{Ru}^{5-2p}\mathrm{Sr}_{2}^{2+}\mathrm{Gd}^{3+}\mathrm{Cu}_{2}^{2+p}\mathrm{O}_{8}^{2-}$$
(32)

with $p \approx 0.08$. Thus, the hole concentration in the CuO₂ layer corresponds to the underdoped region in the phase diagram of HTSC cuprates, which explains the moderate values of T_c . The study of the isotope effect when ¹⁸O is substituted for ¹⁶O shows that for the superconducting transition $\alpha_{SC} = 0.12 \pm 0.04$ [161], which is close to the values for other underdoped cuprates. At the same time, the shift in the temperature of the magnetic transition is very small, $\alpha_M \approx 0.02$, in contrast to the large isotope effect in the transition to the FM phase in the magnetics La_{1-x}Ca_xMnO₃ [162].

The picture of the coexistence of superconductivity and ferromagnetism in Ru-1212 that had formed by the middle of 2002 was completely shattered by the results of the neutron diffraction studies conducted by Lynn et al. [163], who found no FM phase but discovered AFM ordering of ruthenium spins. Attempts to reconcile the data of magnetic measurements, which indicate the existence of macroscopic magnetization in the sample, with the results of neutron diffraction studies [163] using the hypothesis of weak ferromagnetism with two canted AFM sublattices and a net macroscopic magnetization M do not agree with the results of Lynn et al. [163], according to which $M = 0 \pm 0.1 \mu_{\rm B}$. The band structure calculations by Nakamura et al. [164] with a modified crystal lattice for Ru-1212, in which the RuO₆ octahedrons are rotated through an angle $\varphi \approx 14^{\circ}$ about the c axis showed the advantage of the AFM state over the FM state. Another explanation of the situation was suggested by Chu et al. [165], who assumed that superconducting AFM domains form as a result of phase separation and that in the boundaries between the domains an FM state sets in. With a crystal grain larger than $2-5 \mu m$, such a domain is smaller than 0.3 μm [165]. On the whole, the situation is unclear. No one has yet repeated the neutron diffraction studies of Lynn et al. [163]. Besides, single crystals of rutheno-cuprates are as yet unavailable, and all studies are conducted using polycrystalline samples.

7. Possibilities of practical application of ruthenates

The high sensitivity of triplet superconductivity to the presence of defects and the small values of T_c in Sr₂RuO₄ will hardly make it possible to use the superconducting properties of ruthenates in the near future, although from the viewpoint of materials science this class of materials is very interesting, especially for using them in superconducting electronics. The point is that, in contrast to cuprates, ruthenates are highly stable thermodynamically, while their structural characteristics are close to those of cuprates. For instance, for YBa₂Cu₃O₇ the in-plane lattice parameters are a = 3.82 Å and b = 3.89 Å, and for Sr₂RuO₄ a = b = 3.87 Å.

This fact, when combined with the good metallic properties and high thermal conductivity and thermodynamic stability, makes Sr_2RuO_4 single crystals suitable for use as substrates for epitaxial growth of thin YBa₂Cu₃O₇ films [127]. Additional advantages of Sr_2RuO_4 as a material for substrates are that the single crystals can be grown quite easily by the floating-zone method, they remain tetragonal without structural phase transitions in the entire temperature range required, and they exhibit only a slight temperature dependence of the lattice parameters [9].

The advantages of Sr_2RuO_4 as a metallic substrate were realized in the fabrication of epitaxial SNS heterostructures YBa₂Cu₃O₇/Sr₂RuO₄/YBa₂Cu₃O₇ [50]. Also studied were an SIS heterostructure with an insulating layer, Sr_{1.1}La_{0.9}FeO₄ (a = b = 3.87 Å), and a field-effect transistor based on Sr₂RuO₄ as a gate and on the isostructural oxide Sr_{1.1}La_{0.9}FeO₄ as the insulating layer on which a HTSC Y-123 or BSCCO film is grown.

Thin films of another ruthenate, SrRuO₃, and of solid solutions Sr_{1-x}Ca_xRuO₃ with 0 < x < 1 are more easily fabricated than Sr₂RuO₄ films by the laser sputtering and molecular-beam epitaxy methods [166]. These films proved to be interesting objects when they were combined with ferroelectric and dielectric perovskite oxides, e.g., as electrodes of RAM capacitors using the perovskite (Ba,Sr)TiO₃. Obviously, the possibilities of integrating various oxides with close lattice parameters but different electrical and magnetic properties are very promising.

8. Conclusions

The studies conducted in the last 15 years have presented to solid state physics such interesting classes of materials as cuprates, manganites, and ruthenates. Structurally, these classes are very close to each other, all having quasi-twodimensional layers or packets of coupled layers, but their electronic properties differ considerably. In cuprates, the properties are determined by the competition between antiferromagnetic and singlet superconducting correlations, while in manganites the competition is between ferromagnetic and antiferromagnetic interactions. In ruthenates we are dealing with competition between ferromagnetic, antiferromagnetic, and triplet superconducting fluctuations. Another difference between ruthenates on the one hand and cuprates and manganites on the other is that in cuprates and manganites, the phase diagram is determined by doping, i.e., by changes in the electron concentration, while in ruthenates, the change of phases in isoelectronic solid solutions is controlled primarily by angular displacements of the RuO₆ octahedrons. The phase diagrams of doped ruthenates have not yet been thoroughly studied, although interesting examples of phase stabilization at small dopant concentrations are known and have been discussed in this review.

The most interesting property of ruthenates from the fundamental viewpoint is of course the triplet superconductivity of Sr_2RuO_4 , which makes this material similar to superfluid ³He, while in solid state physics it is known to exist in heavy-fermion superconductors of the UPt₃ type, in quasi-one-dimensional superconductors, and, possibly, in the recently discovered ferromagnetic superconductors UGe₂ [167]. The chirality of the superconducting state of Sr_2RuO_4 may lead to various interesting effects, such as the quantum Hall effect even in the absence of magnetic field [168]. The spontaneous quantum Hall effect emerges as a response to

supercurrent flow. The effect is extremely weak and is difficult ⁴⁰²³⁹. doi>40. to detect in experiments.

Another open question is the possibility of triplet superconductivity in Sr₃Ru₂O₇. To answer it, we must learn to 242. grow perfect single crystals with a residual resistivity $\rho_{\rm res} < 1 \ \mu\Omega$ cm. A unique possibility is presented by ruthe- ω^2 43. nates from the viewpoint of integrating them with cuprates, 44. both in natural superlattices of rutheno-cuprates of the Ru-1212 and Ru-1222 type and in artificially fabricated SNS and SIS heterostructures, which is also interesting from the 43. application standpoint. doi>47

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